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Concise Certificate Chemistry

David Abbott

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Concise Certificate Chemistry

ALSO BY DAVID ABBOTT

Revision Chemistry for Sixth Forms
An Introduction to Chromatography (with R. S. Andrews)
An Introduction to Reaction Kinetics

Concise Certificate Chemistry

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Preface

This book was planned as a companion to *Revision Chemistry for Sixth Forms*, published in July 1964. It is intended (a) as a revision book and (b) as a general class book for students preparing for the General Certificate of Education examination at Ordinary Level, or an equivalent standard. The book presents an up-to-date picture of chemistry at this level. Ionic equations are used where applicable, instead of the more outmoded molecular ones, and the writing of chemical formulae is based on types of chemical bond. Topics included which do not normally find their way into books at this level are chromatography, chemical equilibrium and factors affecting chemical change, organic chemistry (very elementary), the electronic theory of valency and types of bond, molarities, etc. The concept of an acid and a base adopted is one of a proton donor or proton acceptor—is it not time that the 'replaceable hydrogen' definition disappeared? The standard definitions of equivalent weights of acids and bases are adjusted to cope with the definitions of an acid and a base proposed. A short selection of questions is given at the end of each chapter to help the student during his or her revision. A chapter is included on qualitative analysis—gas testing, tests for cations and anions, and so on.

The best advice is to start revision *early* and to make sure that every argument is understood. In preparing this book, I have tried to concentrate on *understanding facts*, as well as merely giving the relevant ones. This is a book of *chemical principles* rather than a book including all the possible facts.

I shall appreciate any comments on the book which are sent to me, and hope that it will prove of some value to the students for whom it is intended.

DAVID ABBOTT
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1 Elements, Mixtures and Compounds

1.1 PHYSICAL AND CHEMICAL PROPERTIES

The most obvious properties of a substance are those which affect the senses, i.e. smell, taste, touch, sight and hearing. These are said to be physical properties, although there is now reason to believe that smell involves chemical reaction. Physical properties which can be *measured* are often of more value, e.g. boiling point, freezing point, density (mass per unit volume), specific heat, and solubility in a given solvent. Thus a colourless, odourless liquid with a boiling point of 100°C, a freezing point of 0°C and a density of 1 g/cm^3 will certainly be water. When dealing with metals, electrical and thermal conductivity are important physical properties.

Chemistry is concerned mainly with chemical properties, i.e. the behaviour of different substances with air, water, acids, alkalis, or when heated alone.

1.2 PHYSICAL AND CHEMICAL CHANGES

From the results of a large number of experiments involving different substances, it is possible to deduce the characteristic features associated with physical and chemical changes.

Table 1.1

	Physical changes	*Chemical changes*
1.	A new substance is never formed	A new substance is always formed
2.	Little or no heat change	Often considerable heat change
3.	It is usually easy to reverse the process, thereby regaining the original material	It is usually very difficult to reverse the process
4.	No alteration in weight	Appears to be an alteration in weight, although the weight has really been redistributed

Examples of physical changes include all cases of melting of solids or solidification of liquids, vaporization of liquids or liquefaction of gases, magnetization of iron, the process of solution, the passage of electricity along a wire.

Examples of chemical changes include the rusting of iron, the burning of a candle, the burning of coal in an open grate, the combination of iron filings and sulphur when heated together.

Can you classify the following?

(*a*) A stone rolls down a hill; (*b*) Sugar dissolves in water; (*c*) Petrol burns in an engine; (*d*) A piece of glass is broken; (*e*) Mercuric oxide is heated to give mercury and oxygen.

1.3 THE STATES (PHASES) OF MATTER

Matter (i.e. anything which can be weighed) consists of three states, solid, liquid and gas or vapour. A solid has a definite volume and a definite shape and it usually requires a considerable force to alter its volume or its shape. A liquid has a definite volume but takes up the shape of its container. A gas takes up both the volume and shape of its container.

The term vapour is used for the gaseous form of a substance which is normally a liquid or a solid. Thus nitrogen is a gas since it is gaseous at room temperature while the gaseous form of nitric acid is called nitric acid vapour.

Substances can change state as follows:

$$\begin{tikzcd}[column sep=huge]
\text{SOLID} \arrow[r, shift left, "\text{melting, fusing}"] \arrow[rr, leftrightarrow, bend left=30, "\text{sublimation}"] & \text{LIQUID} \arrow[l, shift left, "\substack{\text{freezing, solidifying}\\ \text{(at the melting or}\\ \text{freezing point)}}"] \arrow[r, shift left, "\text{evaporation, boiling}"] & \text{GAS OR VAPOUR} \arrow[l, shift left, "\substack{\text{condensing, liquefying}\\ \text{(at the boiling point)}}"]
\end{tikzcd}$$

Lead, water and oxygen are generally regarded as solid, liquid and gas respectively but they can exist in all three states depending on their temperature. Thus,

$$\text{Lead} \xleftrightarrow{327{\cdot}5^{\circ}\mathrm{C}} \text{Liquid lead} \xleftrightarrow{1620^{\circ}\mathrm{C}} \text{Lead vapour}$$

$$\text{Ice} \xleftrightarrow{0^{\circ}\mathrm{C}} \text{Water} \xleftrightarrow{100^{\circ}\mathrm{C}} \text{Steam}$$

$$\text{Solid oxygen} \xleftrightarrow{-218{\cdot}4^{\circ}\mathrm{C}} \text{Liquid oxygen} \xleftrightarrow{-183^{\circ}\mathrm{C}} \text{Oxygen gas}$$

Evaporation is the slow change of a substance from the liquid to the vapour state at temperatures below the boiling point. Heat is absorbed when a liquid evaporates and the rate of evaporation increases with increase of temperature (wet clothes dry more rapidly on a hot day).

Boiling can be regarded as a rapid evaporation.

It should be pointed out that evaporation really refers to passage into *free space*. If a liquid evaporates into a confined space, the space eventually becomes *saturated* with the vapour; there is, in fact, an equilibrium existing between the vapour and the liquid and (as is discussed below) a *maximum* pressure is exerted called the saturated vapour pressure. Wet clothes do not dry in a closed container—why?

If the vacuum in a mercury barometer is saturated with vapour of a liquid, the vapour exerts a pressure which can be measured by the fall in mercury level; this is called the saturated vapour pressure of the liquid. The vapour pressure of a liquid increases with temperature until it reaches atmospheric pressure; at this point the liquid boils, i.e. the boiling point of a liquid is the point at which the saturated vapour pressure equals the external pressure. A liquid with a high vapour pressure at room temperature is said to be very *volatile*.

Saturated vapour pressure

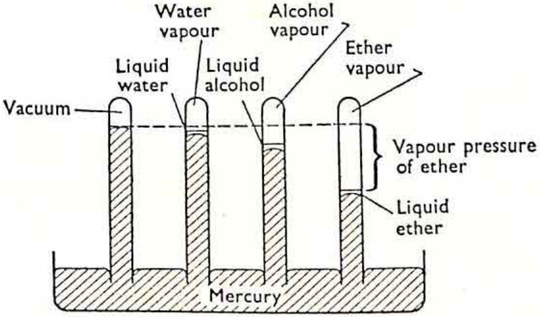


FIG. 1.1

Solids normally exert only small vapour pressures but, in a few cases, the solid can exert an appreciable vapour pressure so that the vapour pressure is equal to the externally applied pressure below the melting point. This means that the solid evaporates before it melts, i.e. it changes directly from solid to vapour and vice versa without passing through the liquid state. This is called sublimation. Examples include ammonium chloride, naphthalene, carbon dioxide and iodine.

Apparatuses suitable for determining the melting and boiling point of a substance are shown in fig. 1.2.

Not all substances exist in all three states of matter; the change in temperature needed to bring about a change of state often decomposes a substance, e.g. liquid calcium carbonate is not known.

Determination of melting point and boiling point

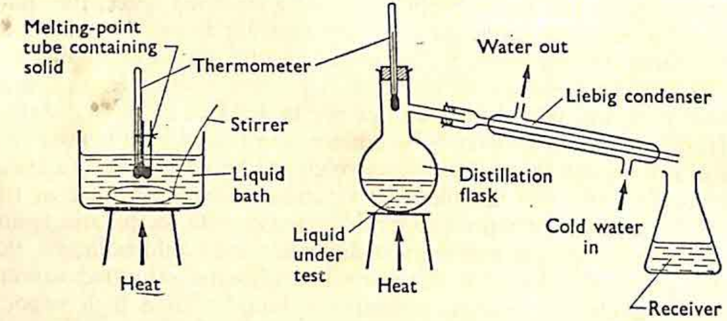


FIG. 1.2

1.4 ELEMENTS, MIXTURES AND COMPOUNDS

Boyle suggested that an element is a substance which cannot be split into something simpler by a chemical or physical change. This definition is unsatisfactory for radioactive elements (see 2.5).

There are now (1966) 104 elements known. The majority of them were discovered during the nineteenth century although some (e.g. silver, gold, tin, sulphur, carbon, iron, lead) have been known since prehistoric times. Elements can be either solids, liquids or gases under normal conditions.

Table 1.2

Solids		*Liquids*	*Gases*
Copper	Tin	Bromine	Oxygen
Silver	Aluminium	Mercury	Nitrogen
Iron	Sodium		Hydrogen
Zinc	Lead		Chlorine
Lead	Carbon		Argon

Not all the naturally occurring elements are found in the free state, but they are generally found in the form of a compound (see later). The approximate percentages by weight of some of the more commonly occurring elements is shown in table 1.3.

Table 1.3

Abundance of elements in the Earth's crust (plus air and water)

Oxygen 50%
(in water, free in air,
and as oxides)

Silicon 27%
(as sand, clay, silicate minerals in rocks)
Aluminium 7%
Iron 4%
Calcium 3%
Sodium 2·5%
Potassium 2·5%
Magnesium 2%
Titanium 0·5%
Hydrogen 0·2%
Chlorine 0·2%
Rest 2·1%

About 77 per cent of the Earth's crust is occupied by non-metals and 23 per cent by metals. Most metals occur as compounds called *minerals* which are present in naturally occurring *ores*, e.g. Galena contains lead sulphide, Haematite contains iron (ferric) oxide, Bauxite contains aluminium oxide, Cinnabar contains mercury (mercuric) sulphide.

The early classification of elements as either metals or non-metals, though of historical importance, is not entirely satisfactory since some elements are difficult to place in either class, e.g. arsenic, antimony, selenium, germanium. It is, however, still useful to know the properties characteristic of typically metallic and typically non-metallic elements.

Table 1.4

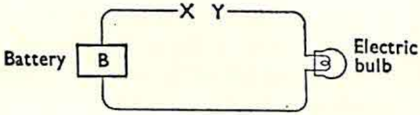
Metals	*Non-metals*
1. PHYSICAL PROPERTIES	
(*a*) Lustrous and can be polished	Non-lustrous, but graphite (carbon) and iodine have a metallic sheen
(*b*) Malleable—can be beaten into sheets	Brittle
(*c*) Ductile—can be drawn into wires	Not ductile
(*d*) Good electrical and thermal conductors	Poor conductors of both heat and electricity, although graphite is a moderate conductor of both

Metals	*Non-metals*
(*e*) Sonorous when struck	Not sonorous
(*f*) High tensile strength	Cannot withstand stress
(*g*) High density, but there are exceptions such as sodium, potassium, calcium, aluminium, magnesium	Low density, but there are exceptions such as iodine
(*h*) High melting point, but there are exceptions, e.g. mercury, tin, potassium	Low melting points, but there are exceptions, e.g. carbon, silicon, boron

2. CHEMICAL PROPERTIES

(*a*) At least one oxide is basic (see 7.9)	Oxides are never basic, and usually acidic
(*b*) Usually react with dilute sulphuric or hydrochloric acid to give a salt (see 6.8) plus hydrogen	No reaction with these dilute acids

Electrical conductivity of metals and non-metals



Connect a piece of iron and sulphur separately across XY. The bulb lights up for iron, but not for sulphur.

(*c*) Chlorides are generally solids and ionic compounds (see 2.9)	Chlorides are generally volatile liquids which can usually be decomposed by water
(*d*) Metals form solid sulphates which are ionic compounds (see 2.9)	Non-metals form no sulphates
(*e*) Form positive ions which move to the cathode on electrolysis (see 3.1)	Form negative ions, especially when forming part of an acid radical (see 2.8), and move to the anode on electrolysis

Chemical compounds result from the combination of elements in certain definite proportions. A compound can be defined as a substance containing two or more elements chemically joined together in such a manner that the properties of the elements are completely altered. Examples include water (hydrogen combined with oxygen), common salt (sodium combined with chlorine), and clay (aluminium, silicon, oxygen and hydrogen combined together).

In compounds, the elements are held together by chemical bonds (see 2.9).

A mixture consists of any number of elements or compounds, or elements and compounds all jumbled up together, the elements and compounds not being bonded together in any way and each retaining its own individual properties.

Examples include air (nitrogen about 80 per cent by volume, oxygen about 20 per cent, carbon dioxide about 0·03 per cent, Rare Gases, i.e. argon, neon, helium, krypton, xenon and radon, about 1 per cent, together with variable amounts of water vapour, bacteria, dust, etc.), brine (sodium chloride and water), brass (an alloy of copper and zinc), and bronze (an alloy of copper and tin).

The characteristic differences between mixtures and compounds are given in table 1.5A.

Table 1.5A

	MIXTURES	COMPOUNDS
1.	The constituents can be separated easily by methods not involving a chemical change	The constituents can only be separated by chemical means
2.	The constituents can be present in any proportion	Formed from elements by chemical combination in definite proportions only
3.	Their properties are intermediate between those of the constituents, and in proportion to the amount of each present	Their properties need bear no resemblance to those of the constituent elements and are characteristic of the compound
4.	Their formation involves a physical change and little or no heat change is produced	There is often considerable heat change during formation. Exothermic compounds are those formed from their elements with the evolution of heat. Endothermic compounds are those formed with the absorption of heat

Table 1.5B shows the properties of a mixture of iron filings and sulphur compared with those of ferrous sulphide, formed when the elements are heated together in the correct proportions by weight.

Table 1.5B

Mixture of iron and sulphur	*Compound, ferrous sulphide*
No heat change on formation	Heat change when formed
Composition variable from almost 100% iron to almost 100% sulphur	Fixed composition; 1 atom of iron to 1 atom of sulphur, or 7 grams of iron to 4 grams of sulphur
Variable colour	Black
Variable physical properties, e.g. density	Fixed physical properties
Iron portion reacts with dil. hydrochloric acid to produce hydrogen; sulphur portion unchanged	Reacts with dil. hydrochloric acid to form hydrogen sulphide
Sulphur portion soluble in carbon disulphide, or xylol	Insoluble in carbon disulphide or xylol
Partially magnetic	Non-magnetic
Separate component parts visible under microscope, i.e. not homogeneous	No separate component parts visible under microscope, i.e. homogeneous

Question

Classify the following as elements, mixtures or compounds: diamond, coal, petroleum, common salt, sand. Give reasons to support your answer.

1.5 TYPES OF CHEMICAL REACTION

(a) Direct combination

Two or more elements and/or compounds combine to give one compound, for example:

$$\text{iron} + \text{sulphur} \xrightarrow{\text{heat}} \text{ferrous sulphide}$$

$$\text{sulphur dioxide} + \text{oxygen} \rightarrow \text{sulphur trioxide}$$

$$\text{hydrogen} + \text{chlorine} \rightarrow \text{hydrogen chloride}$$

(b) Thermal decomposition

A compound decomposes on heating alone, for example:

potassium chlorate → potassium chloride + oxygen
lead nitrate → lead monoxide + nitrogen dioxide + oxygen

(c) Thermal dissociation

A compound decomposes on heating and the products recombine on cooling to give the original compound again, i.e. it is reversible thermal decomposition, for example:

ammonium chloride ⇌ ammonia + hydrogen chloride
phosphorus pentachloride ⇌ phosphorus trichloride + chlorine
calcium carbonate ⇌ calcium oxide + carbon dioxide

(d) Double decomposition

These have the general type

$$AX + BY \rightarrow AY + BX$$

where A and B are metallic radicals (see 2.8) and X and Y are acidic radicals (see 2.8). The best known examples are when AY or BX is a gas or a sparingly soluble substance. In the latter case, the reaction is called a precipitation reaction, the insoluble substance being a precipitate. Precipitation reactions can be written in terms of ions (see 2.9), for example:

Gas formed	sodium chloride	+	sulphuric acid (conc.)	→	sodium bisulphate	+	hydrogen↑ chloride
Precipitate formed	silver nitrate	+	sodium chloride	→	sodium nitrate	+	silver ↓ chloride

(e) Replacement (displacement) reactions

Here one element or radical is replaced by another element or radical.

$$A + BX \rightarrow AX + B$$

For example:

zinc + cupric sulphate → zinc sulphate + copper
zinc + sulphuric acid → zinc sulphate + hydrogen↑
chlorine + potassium iodide → potassium chloride + iodine

(f) Reversible reactions (see 16.1)

(g) Exothermic reactions (in which heat is *evolved*, thereby reducing the energy of the system) and Endothermic reactions (in which heat is *absorbed*, thereby increasing the energy of the system).

For example:

$$\text{nitrogen} + \text{hydrogen} \rightleftharpoons \text{ammonia (heat evolved)}$$
$$\text{nitrogen} + \text{oxygen} \rightleftharpoons \text{nitric oxide (heat absorbed)}$$

You can study the heat energy changes involved in some simple chemical reactions by carrying out the following reactions in polythene bottles and measuring the rise in temperature (use $2M$ (M = molar, see 17.3) solutions): sodium hydroxide/hydrochloric acid, sodium hydroxide/acetic acid, iron/cupric sulphate, silver nitrate/hydrochloric acid.

The significance of these heats of reaction lies in the making and breaking of chemical bonds (see ch. 2).

1.6 SEPARATION OF MIXTURES

(a) Solid suspended in a liquid

Filtration

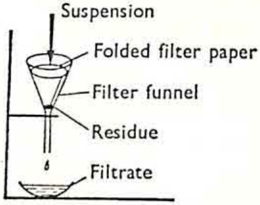


FIG. 1.3

Purification of water

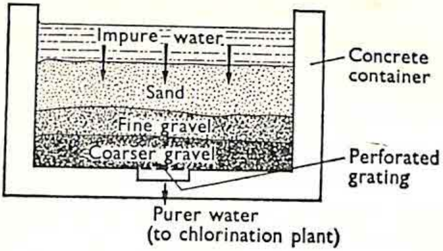


FIG. 1.4

Example: The separation of sand and salt; the salt is dissolved in water leaving the sand undissolved, the sand filtered off, and the salt solution evaporated to give solid salt.

Of commercial importance is the purification of water for drinking purposes in a filter bed.

(b) Separation of a solution into the solute and solvent (see 14.1)

1. *By evaporation to dryness.* This method never gives crystals of the solid (since the solid is formed too rapidly) and the solvent is lost as vapour.
2. *By crystallization.* The solution is warmed in an evaporating basin until saturated (see 14.1). This can be ascertained by placing a *cold* glass rod in the solution from time to time, removing it, and noticing whether or not crystallization takes place as the solution cools. The solution is then placed on one side to allow crystals to form.
3. *By distillation* (see fig. 1.2). Here the solvent can be recovered from a solution, the solute remaining (non-crystalline) in the distilling flask.

Evaporation

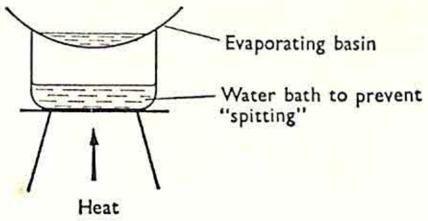


FIG. 1.5

(c) Separation of two or more miscible liquids with different boiling points

The process used is fractional distillation. The principle is that the mixture is heated until the liquid of lowest boiling point has been converted to the vapour state, this being condensed back to the liquid by a condenser. On raising the temperature further, the liquid with next lowest boiling point is converted to the vapour state and this is condensed back to the liquid in another receiver, and so on, the process being continuous. The efficiency of the separation is aided with a *fractionating column*, which consists of a glass column containing a series of glass rods or beads to act as 'arrest points'. Suppose that two liquids of different boiling point, such as acetone (b.p. 58°C) and water (b.p. 100°C) are to be separated. When the liquid is heated, the vapour containing mainly acetone passes up the column. The arrest-points

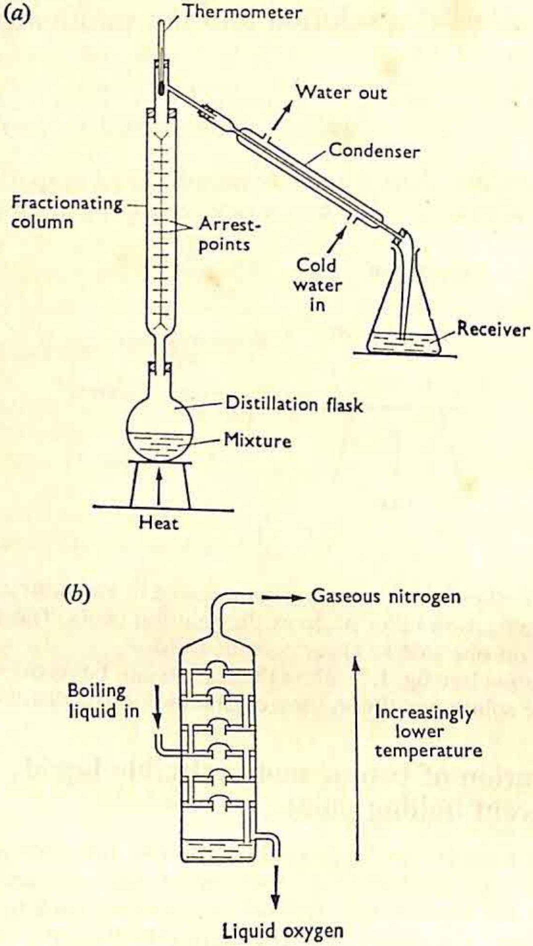


FIG. 1.6

allow liquid to condense on them and the less volatile liquid (water) falls back into the flask. The liquid on a given arrest-point is raised to the boiling point by heat evolved when more liquid condenses there. As the mixture of vapours passes up the column, it gets richer and richer in the more volatile constituent (acetone) and the liquid in the flask gets richer and richer in the less volatile constituent (water). The method can be applied to mixtures of more than two liquids, e.g. the separation of liquid air into (mainly) nitrogen (b.p. −196°C), argon (b.p. −186°C) and oxygen (b.p. −183°C), coal tar into a variety of products (benzene, toluene, xylenes, phenols, etc.), and crude oil into a variety of product (petrols, paraffin oils, lubricating oils, etc.).

(d) Separation of immiscible liquids: a separating funnel is used.

Separating funnel

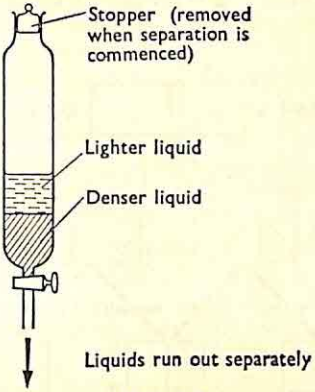

Stopper (removed when separation is commenced)
Lighter liquid
Denser liquid
Liquids run out separately

FIG. 1.7

Examples are benzene and water, mercury and water.

(e) Separation of two or more solids which are soluble in a given solvent

The process of fractional crystallization is used which relies on the difference in solubilities of the solids in the given solvent at various temperatures. As an example, consider a mixture of 20 grams of potassium nitrate with 18 grams of potassium chlorate. The solubilities concerned are

	Nitrate	*Chlorate*
Solubility at 50°C	86 grams	18 grams
Solubility at 20°C	31 grams	8 grams

If the mixture is dissolved in 100 grams of water at 50°C the solution will be just saturated with potassium chlorate but not saturated with potassium nitrate. On cooling to 20°C, 10 (18 − 8) grams of potassium chlorate will separate out as crystals but no potassium nitrate will come out of solution for, even at 20°C, the solution is still not saturated with potassium nitrate. Thus potassium chlorate is obtained from the mixture.

This method of purification is widely used, in a rather more complicated way, but only if it is not possible to find a solvent which will dissolve one component of a mixture and not the others.

A diagrammatic representation of fractional crystallization of a mixture of A and B is as follows. A is slightly less soluble than B and the relative amounts of A and B are shown by shaded and non-shaded areas.

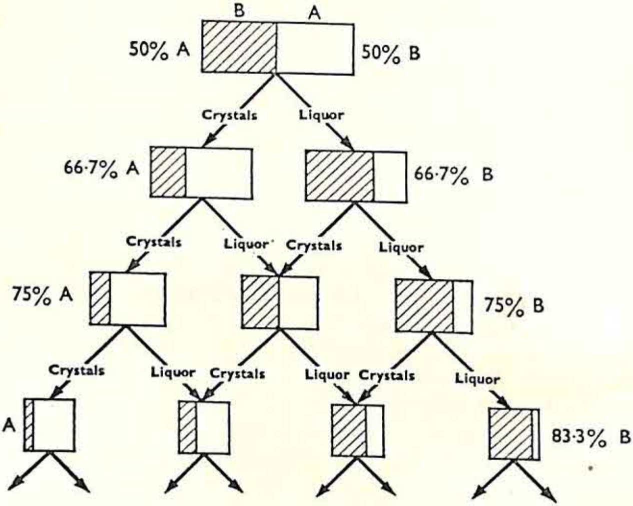


FIG. 1.8

The mixture is dissolved in hot solvent, A being slightly less soluble than B. Amounts are taken such that, when cooled, about half the dissolved solid crystallizes out. The crystals will be enriched in A (less soluble), whilst the 'mother liquor' will be enriched in B (more soluble). The enriched crystals are redissolved and the solution recrystallized, yielding a crop of crystals still richer in A, and a 'mother liquor' still richer in B. The original 'mother liquor' gives, on evaporation and recrystallization, yet another solid (rich in A) and liquid (rich in B).

By repeated treatment, as summarised in the diagram, it is possible to obtain more or less pure A and B, but the crystallization may have to be repeated many times.

(f) Chromatography

Plants and animals are sources of many chemicals. Grass is green and flowers are coloured because there is a green material or another coloured material in them. This coloured substance cannot be extracted with water, but a non-aqueous solvent (see 14.1), e.g. acetone or alcohol will do it. The question now arises, 'How do we know whether these coloured substances are just one thing or a mixture?' If you have ever spilt ink blots on blotting paper, you will have noticed that the pigment partially separates into two or more colours. This gives us a clue as to the method for investigating coloured substances in grass and flower extracts.

Chromatography is a technique for the separation and identification of substances present in complex mixtures. For example, when a protein is heated with an acid, the protein is degraded to a complicated mixture of substances which cannot be separated satisfactorily by any of the methods previously described. In the most common forms of chromatography, the mixture to be separated is dissolved in a suitable solvent and fractionated by the paper or column method.

In paper chromatography, which is used for relatively small quantities of material, a spot of the solution containing the mixture is applied to the base line drawn in pencil on a strip of filter paper. Separation is effected by placing the paper (after the spot has dried) in a suitable solvent which flows over the spot and carries the components different distances along the paper. The distance moved by a given substance in the mixture is independent of the other substances present and is characteristic of the substance. It is normally quoted as an R_F value, this being the distance travelled by the substance divided by the distance travelled by the solvent front. In some cases, the solvent front has to run off the end of the paper in order to effect a separation, and the migration has then to be quoted as an R_X value which is the distance travelled by the substance divided by the distance travelled by a standard substance X.

The word chromatography means literally 'colour writing', since the original substances to be separated by the technique were all naturally coloured. The technique can now be applied to colourless substances, but they have to be located on the paper after separation. In the most common method of location, the paper is dried and sprayed with a suitable reagent which converts the colourless compounds into coloured ones. The finished paper is called a *paper chromatogram.*

If the solution containing the mixture is applied as a streak to the base line of the filter paper, and the chromatogram developed in the chosen solvent, strips can be cut from the edges of the dried paper, sprayed to locate the positions of the bands containing the various components, and then fitted back into their correct positions on the paper. In this way the areas of the paper containing the separated components can be mapped out, cut out separately, and the components extracted from the strips of paper with a suitable solvent.

There are two methods by which paper chromatography can be carried out, these being the descending and ascending methods (see fig. 1.9).

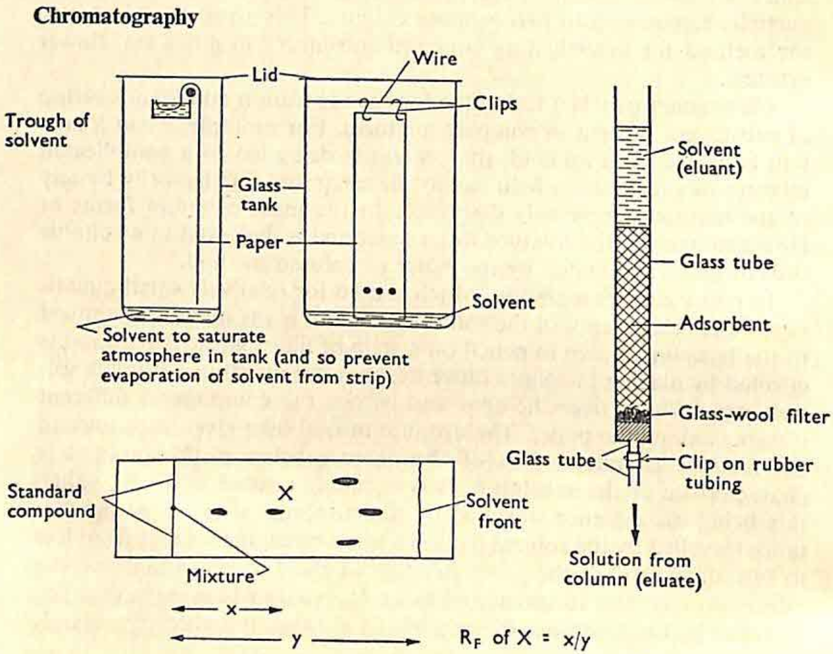

Chromatography

FIG. 1.9

In column chromatography, the solution containing the mixture is poured on to a column of a suitable substance, called an *adsorbent*, e.g. cellulose powder, alumina, silica, charcoal. The adsorbent is packed into a glass tube as a slurry in the solvent which is to be used for separation. The chromatogram is developed by pouring the separating solvent down the column. If the adsorbent is white, and the substances in the mixture are naturally coloured, a series of coloured bands will form at different distances from the top of the column. If the adsorbent is dark (e.g. charcoal) or the substances are not naturally coloured, a different method of location has to be used (you will find this discussed in a more advanced textbook).

Some of the above topics are illustrated in fig. 1.9A.

Chromatography, like fractional crystallization, is a *fractionation* process.

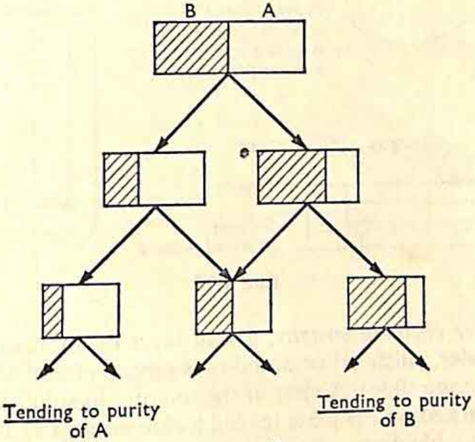


FIG. 1.10

Chromatography is a new technique and has made a phenomenal advance during the few years it has been applied. Probably no other new technique has made such a spectacular advance.

Separations for you to try

1. Separate an acetone extract of spinach or grass leaves on a column of magnesia (magnesium oxide) using cyclohexane as developing solvent. Notice the separation of green (chlorophylls), yellow (xanthophylls) and orange (carotenes) bands.
2. Separate screened methyl orange indicator on a column of alumina (aluminium oxide) using ethyl alcohol (ethanol) as solvent. Notice the separation of yellow and blue bands.
3. Carry out very simple separations of the pigments in (*a*) screened methyl orange, (*b*) commercial blue-black ink as shown in fig. 1.11(a).
4. Separate a mixture of lead nitrate and silver nitrate (dissolved in

water) by ascending paper chromatography in a boiling tube (fig. 1.11(b)). Develop in distilled water, remove the paper and dry it, and locate the compounds by dipping the paper in potassium chromate solution (lead chromate is yellow, silver chromate orange).

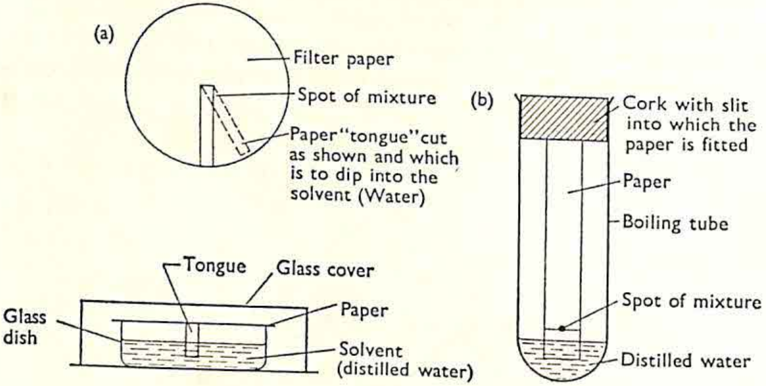

(a)
Filter paper
Spot of mixture
Paper "tongue" cut as shown and which is to dip into the solvent (Water)
Tongue
Glass cover
Glass dish
Paper
Solvent (distilled water)
(b)
Cork with slit into which the paper is fitted
Paper
Boiling tube
Spot of mixture
Distilled water

FIG. 1.11

In *thin layer chromatography*, a thin layer of an adsorbent such as cellulose powder, silica gel or alumina is spread *evenly* on a glass plate (e.g. a microscope slide). A spot of the mixture in solution is placed on a base line marked on the plate (called a *chromatoplate*) and this is then placed in a suitable developing solvent. The dried plate is then sprayed with a suitable reagent (if the compounds are not naturally coloured) as in paper chromatography.

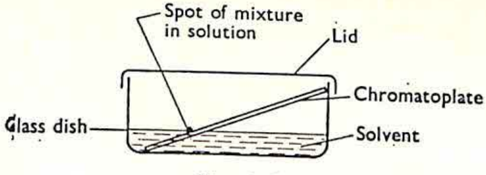


FIG. 1.12

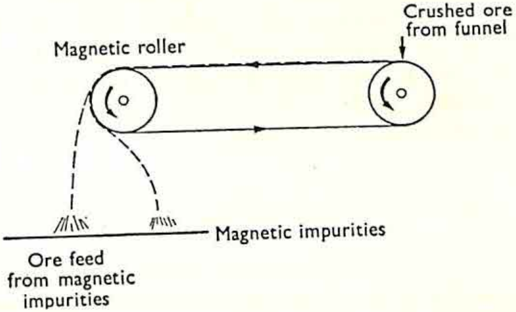
GAS CHROMATOGRAPHY

It is possible to separate mixtures of gases or vapours by chromatography. A small sample of the mixture is injected into a stream of an inert 'carrier gas' (e.g. nitrogen, argon, hydrogen) which carries it into a column packed with a medium suitable for retarding (to different extents) the flow of individual components as they flow through it.

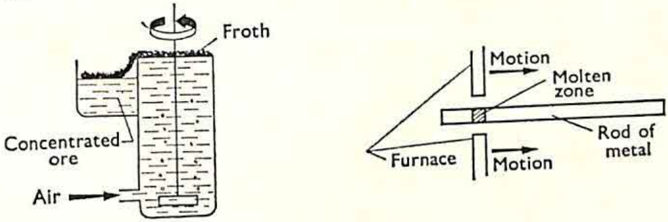
The separated components emerge from the column at different intervals of time from the start of the separation (this time being characteristic of a given component) and pass through some form of detector. This consists of a device which can move a self-recording pen along a moving roll of paper, producing the chromatogram.

Typical examples of the use of gas chromatography are the analysis of petrols and petroleum gases, the analysis of food oils and flavourings, and for following the course of reactions in organic chemistry (see 10.3).

Chromatography is therefore an analytical procedure for the separation of solutes in which separation is effected by a difference in rate of movement through some porous medium, movement being caused by a flow of solvent.



Electromagnetic separation



Ore flotation

Zone refining

FIG. 1.13

(g) Magnetic separation

This is used to separate magnetic and non-magnetic materials, e.g. in the removal of magnetic impurities from tinstone. The crushed ore is allowed to move along a travelling belt which passes over a magnetic roller. The magnetic impurities are pulled over towards the roller and form a separate pile.

(h) Froth flotation

This involves separation of ores from earthy impurities. This is important for concentrating sulphide ores. The finely pulverized ore is mixed with water and some chemical frothing agent added. When air is blown into the mixture, a froth is formed and the earthy material is 'wetted' and sinks. The sulphide particles rise to the surface with the froth where they can be skimmed off into a container. Acid is added to break up the froth and the ore filtered and dried.

(i) Zone refining of metals

This is used on a small scale to give metals in a high state of purity. An impure molten metal gives pure crystals on solidifying. The rod of metal is melted over a very narrow region at one end, in a furnace. The molten region is transferred from one end of the rod to the other by slowly moving the furnace. Impurities collect in the molten zone and are swept to one end of the rod.

Questions

1. A man grows three flowers, one red, one blue and one violet. He wishes to show that the violet one has a colour composed of a mixture of the red and blue colours, as opposed to a single violet colour. Devise an experiment by which he might do this.
2. Give a brief account of (*a*) chromatography, (*b*) fractional distillation, (*c*) fractional crystallization.

~~2017. 5-09~~/

2 Atomic Structure, Formulae and Bonds

2.1 THE ATOMIC THEORY (DALTON, 1807)

(*a*) All elements are composed of small particles called atoms which are indivisible and indestructible.

(*b*) All atoms of the same element are identical, e.g. in weight, but are different from atoms of other elements.

(*c*) Chemical compounds are formed by the union of small whole numbers of atoms to give compound-atoms, all compound atoms of a particular compound being identical.

Modifications

(*a*) Atoms are divisible and, in certain circumstances, destructible, although neither process occurs in a normal chemical change.

(*b*) All atoms of the same element do not necessarily have equal weights. Atoms of the same element with different atomic weights are called *isotopes*.

(*c*) Compound-atoms are called *molecules*.

The atomic theory could account for the laws of chemical combination:

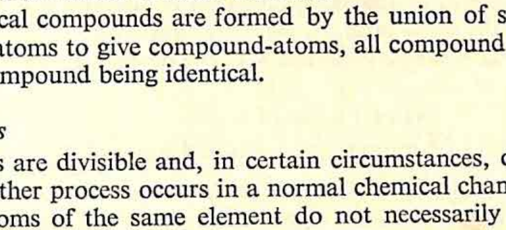


FIG. 2.1

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(a) The law of conservation of mass (Lavoisier, 1774)

Matter is neither created nor destroyed during a chemical reaction. When chemicals react there is a rearrangement of the atoms but, since atoms can neither be created nor destroyed, the total mass remains un-

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altered. The law is tested by carrying out a reaction (such as that between silver nitrate and hydrochloric acid solutions to give silver chloride and nitric acid, or between mercuric chloride and potassium iodide solutions to give mercuric iodide and potassium chloride) and weighing the reaction vessel before and after reaction.

$$\overbrace{Ag^+ + NO_3^-} + \overbrace{H^+ + Cl^-} \rightarrow AgCl\downarrow + \overbrace{H^+ + NO_3^-}$$

(b) The law of definite proportions (constant composition) (Proust, 1799)

All pure samples of the same chemical compound contain the same elements in the same proportions by weight.

In a simple binary compound XY, the percentage by weight of X is given by

$$\frac{\text{Wt of 1 atom of X}}{\text{Wt of 1 atom of X} + \text{Wt of 1 atom of Y}} \times 100$$

The percentage by weight of Y is given by a similar expression. As all X atoms have the same weight and all Y atoms have the same weight (for ordinary work, isotopes exert no material influence), it follows that the percentage of X or Y in a pure sample of XY is a constant.

The law is tested by preparing several samples (by different methods) of one chemical compound (e.g. cupric oxide) and analysing it to determine the percentage composition.

It is now recognized that the composition of some compounds is variable. Such compounds are known as *Berthollide compounds* and are said to be *non-stoichiometric*, stoichiometry being an old-fashioned word for that part of chemistry which deals with gravimetric or volumetric composition of substances. Ferrous oxide and ferrous sulphide are both non-stoichiometric compounds.

(c) The law of multiple proportions (Dalton, 1803)

If two elements combine together to form more than one chemical compound, the various weights of one element which combine with a fixed weight of the other are in numerically simple proportions.

For example, in cuprous oxide one atom of oxygen combines with *two* of copper while in cupric oxide one atom of oxygen combines with *one* of copper.

The law is tested by carrying out an analysis of the several compounds formed by two elements, in order to determine the ratio (by weight) of the elements combined in each compound.

The argument can be applied quite generally; examples are:

N_2O	NO	NO_2	H_2O	H_2O_2
Nitrous oxide	Nitric oxide	Nitrogen dioxide	Water	Hydrogen peroxide

Cu_2O	CuO	CO	CO_2
Cuprous oxide (red)	Cupric oxide (black)	Carbon monoxide	Carbon dioxide

(d) The law of reciprocal proportions (law of equivalents) (Richter, 1792)

This is merely an extension of (*c*). If an element A combines with an element B and also with an element C, and B and C themselves combine together, the proportions in which they do so will be simply related to the weights of B and C combining with a fixed weight of A.

Analysis of methane and water shows that 1 part by weight of hydrogen combines with 3 parts by weight of carbon and 8 parts of oxygen. Therefore it is to be expected that if carbon and oxygen unite, they will do so in the ratio (by weight) of 3 parts of carbon to 8 parts of oxygen, as in fact analysis of carbonic acid gas shows to be the case.

Application of the simple atomic theory to this law is rather complicated. The simplest example concerns three atoms A, B, C which combine to form compounds AB, AC, BC. If the weights of the atoms A, B and C are taken as x, y and z units the state of affairs in the compounds AB, AC and BC is

1 atom of A x units	1 atom of B y units

Compound AB

1 atom of A x units	1 atom of C z units

Compound AC

1 atom of B y units	1 atom of C z units

Compound BC

The weights of B and C combining with x units of A are y and z respectively, and the weights of B and C combining together are in the proportion $y{:}z$. This is in accordance with the law of equivalents.

The atomic theory was not able to account for the law of combining volumes of gases (Gay Lussac, 1808). When gases combine they do so in volumes which bear a simple relationship to one another and to the volumes of any gaseous products provided all volumes are measured under the same conditions of temperature and pressure. For example:

Hydrogen + Chlorine → Hydrogen chloride
1 vol 1 vol 2 vols

On the atomic theory, Dalton supposed that equal volumes of all gases under the same conditions of temperature and pressure contained equal numbers of atoms, i.e.:

$$\underset{\text{hydrogen}}{x \text{ atoms of}} + \underset{\text{chlorine}}{x \text{ atoms of}} \rightarrow \underset{\text{hydrogen chloride}}{2x \text{ compound-atoms of}}$$

$$\underset{\text{hydrogen}}{1 \text{ atom of}} + \underset{\text{chlorine}}{1 \text{ atom of}} \rightarrow \underset{\text{hydrogen chloride}}{2 \text{ compound-atoms of}}$$

If this were true, each atom of hydrogen and chlorine must split into two parts, which is impossible. This logical contradiction was overcome by Avogadro (1811) who suggested that equal volumes of all gases under the same conditions of temperature and pressure contain equal numbers of molecules. He supposed that the molecules of hydrogen and chlorine each contain two atoms and that, when combination of the gases takes place, the molecules split with subsequent combination of the atoms. This overcomes the difficulty of reconciling Gay Lussac's law with the atomic theory.

An *atom* of an element can be defined as the smallest *uncharged* particle of an element which can take part in a chemical reaction.

A *molecule* of an element or compound is the smallest particle of the element or compound which can exist by itself under ordinary conditions or in a free state.

An *element* can then be defined as a substance in which atoms of only one kind are present (add this definition to that given in 1.4).

A *compound* is defined as a substance in which at least two atoms of different kinds are combined together (add this to the definition in 1.4).

The upper limit for the length of an oil molecule can be obtained as follows; this will give you some idea of molecular size.

A 1 cm^3 pipette is filled with camphorated oil and the number of drops contained in 1 cm^3 is counted by allowing the liquid to drain. One drop of oil is then placed on the surface of water, lightly dusted with talc, in a pneumatic trough. An oil film is immediately formed which pushes back the talc particles and the diameter of the film is measured. From the results the thickness of the oil film is determined. The film consists of many oil molecules one above the other. Typical values are as follows:

50 drops of oil contained in 1 cm^3
Diameter of oil film = 18 cm
Volume of drop = $1/50 \text{ cm}^3$
Area of film = $\pi \times 9 \times 9 \text{ cm}^2$
Thickness of film = $1/(50 \times 81 \times \pi) = 0{\cdot}0001 = 10^{-4}$ cm

A more accurate way of determining the volume of an oil drop is to view it on closed-circuit television, measuring the diameter with an adjacent scale.

2.2 INSIDE THE ATOM

Experiments conducted during the nineteenth century on the conductivity of electricity through gases and the bombardment of atoms with high-speed particles have revealed that the atom is composed of a small, hard, dense core called the *nucleus*, in which are particles called protons and neutrons, with electrons in shells (now called energy levels) outside the nucleus. Some properties of these fundamental particles are given in table 2.1.

Table 2.1

Particle	*Electrical charge*	*Mass, relative to that of an atom of hydrogen*
Electron	Unit negative	1/1845
Proton	Unit positive	1
Neutron	Nil	1

The first models of the atom, such as those of Rutherford and Bohr, pictured it as a miniature solar system with electrons rotating around the nucleus. It is now thought that electrons can behave as waves, much like light or sound waves, and that their negative charge is smeared around the nucleus rather than being present in one definite position. Nevertheless, it is usually convenient to adopt the older picture of the atom, especially in studies at the present level, but you will have to accept the modern model of the atom when you have studied chemistry and physics in more detail. The atom of hydrogen is the simplest of all, containing a single electron, a single proton, and no neutrons.

The models of this atom are shown in fig. 2.2.

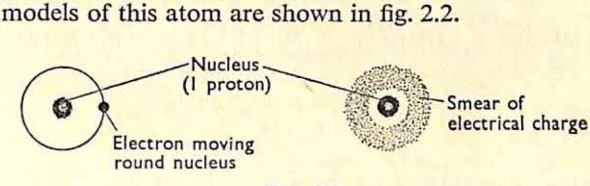


FIG. 2.2

You will almost certainly be familiar with the idea of positive and negative electricity from your studies in electrostatics.

Atoms of different elements have different numbers of electrons and, since the atom is neutral, they have numbers of protons equal to the numbers of electrons. The number of protons in the nucleus of the neutral atom is called the *atomic number* of the element.

It is the number of protons possessed by an atom, and consequently the number of electrons, which is the fundamental determinant of chemical properties of the element.

An idea of atomic size can be obtained from oil-drop experiments, and it is found that atoms must be smaller than 1/10,000,000 cm, i.e. 10 Å (1 angstrom unit = 1 Å = 1/100,000,000 cm).

2.3 THE WEIGHT OF THE ATOM

A single atom is, of course, a very small thing and it has very little weight, but it has been possible in modern times to calculate the actual weight of a single atom of any element. A single hydrogen atom, for example, weighs

0·000,000,000,000,000,000,000,0017 g.

The weight of an atom is really the sum of the weights of all the particles present in it but, since these are so small, the weight is always quoted relative to a fixed standard.

The atomic weight of an element is the weight of 1 atom of the element compared with the weight of 1 atom of a standard element.

The earliest standard was hydrogen (H = 1). This was followed by oxygen (O = 16). The most modern scale proposed is carbon (C = 12).

$$\text{Atomic weight of element} = \frac{\text{Wt of 1 atom of element}}{\frac{1}{12} \times \text{wt of 1 atom of carbon}}$$

The student who has read section 2.4 will realize that the atomic weight of an element is really the *average* weight of its isotopic weights, taking into account their relative abundances. We ought to say, therefore,

$$\begin{matrix}\text{Mass number of isotope}\\ \text{of element}\end{matrix} = \frac{\text{Wt of 1 isotope of element}}{\frac{1}{12} \times \text{wt of 1 isotope of carbon-12}}$$

2.4 ISOTOPES

The definition of an isotope has been given in 2.1. Since the weight of the electron is negligible, and the weights of the proton and neutron are each 1 unit, it might be expected that all atomic weights would be whole numbers. It is therefore surprising to find that the atomic weight of chlorine is 35·5, that of copper is 63·5, and so on. All atoms of the same element must contain the same number of electrons (and protons), but they can differ in their number of *neutrons*. For example, ordinary chlorine contains isotopes having the following compositions:

Chlorine-35: 17 electrons, 17 protons, 18 neutrons
Chlorine-37: 17 electrons, 17 protons, 20 neutrons

Ordinary chlorine is a mixture of these two isotopes in such a proportion that the atomic weight is 35·5.

There are three isotopes of hydrogen, ordinary hydrogen (1 electron, 1 proton, 0 neutrons, atomic weight 1), deuterium (1 electron, 1 proton, 1 neutron, atomic weight 2), tritium (1 electron, 1 proton, 2 neutrons, atomic weight 3). The atomic weight of an isotope is often called its *mass number*.

The way in which isotopes can be written is discussed in 2.7.

2.5 RADIOACTIVITY

The nuclei of elements with atomic weights greater than that of lead (207) are naturally unstable, breaking down at different rates to form other elements and emitting radioactive radiations. Elements like this are said to be radioactive and to *decay* with the formation of other elements. Compounds which contain radioactive elements are also said to be radioactive. Radioactive radiation consists of:

(*a*) alpha (α) particles, which bear a double positive electrical charge and have a mass number of 4 units; they are helium nuclei. They are the least penetrating of the radiations.

(*b*) beta (β) particles, which bear a unit negative electrical charge, have negligible mass, and are high-speed electrons. They are more penetrating than α-particles.

(*c*) gamma (γ) rays, which have no electrical charge, have no mass, and are like X-rays (very penetrating radiation which is produced when electrons are stopped suddenly by a hard target).

	α	β	γ
Relative ionizing power:	10,000	100	1
Relative penetrating power:	1	100	10,000

Radioactive radiations can be 'tracked' by means of a cloud-chamber (Wilson, 1912). The space inside the chamber initially contains dust-free air saturated with water vapour. Sudden expansion of this air, brought about by a rapid movement of a piston, causes cooling so that the air becomes supersaturated (14.1). When the radioactive radiations are passed into the chamber, they cause ions (see 2.9) to be formed by ejection of electrons from atoms in the air inside the chamber. Water droplets are allowed to condense on the ions, and these scatter a beam of light, making the track visible (this can be photographed).

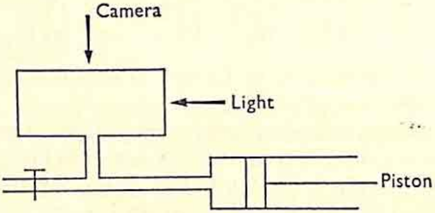


FIG. 2.3

Radioactive radiations can be counted with a Geiger-Müller counter. This consists essentially of a hollow cylinder with a thin metal wire passing along its axis and insulated from the cylinder. The cylinder is filled with a mixture of gases at low pressure, the nature of the gases depending on the use of the counter. The cylinder (or cathode) can be earthed while the central wire (anode) can be raised to a potential of about 1000 volts. Passage of a radioactive radiation through the cylinder enables a pulse of electric current to flow between the wire and cylinder. Such a pulse can be amplified so that it can be recorded on an automatic counter, which records the number of pulses.

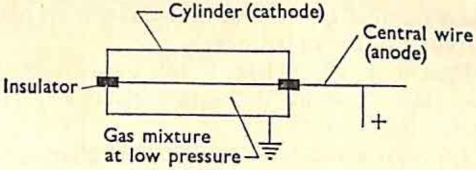


FIG. 2.4

The radioactive radiations can be differentiated by Curie's method (fig. 2.5).

Radioactive substances disintegrate at different rates. A given mass (M) of radium, for example, will be reduced to M/2 in 1590 years; this mass will be reduced to M/4 in another 1590 years, and so on. The time taken for a given mass of a radioactive substance to be reduced to half the amount is called the *half-life* value.

You can examine radioactive decay by a photographic emulsion method. If a photographic plate is exposed to radiation from a thorium salt, and the 'stars' produced are examined under a microscope, the lengths of the tracks can be used to identify the element emitting the α-particles.

Radioactivity can be induced artificially and it is possible, by bombarding certain elements with high-speed particles, to produce radioactive isotopes of other elements. For example, if aluminium is bombarded with α-particles, a radioactive isotope of phosphorus is formed. This type of process is called *transmutation*, and forms the basis for the preparation of elements of atomic weight greater than that of uranium (the transuranium elements).

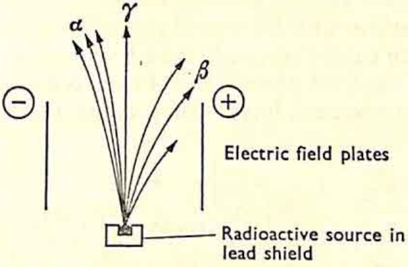


FIG. 2.5

In an atomic or hydrogen bomb explosion, a large number of radioactive isotopes are released, escape into the atmosphere, and are carried away by winds. When the fireball of the explosion touches the ground, radioactive isotopes stick to the fine dust particles, forming 'fall-out'; this is sucked up into the cloud and carried up into the atmosphere. Over a period of time the fall-out settles on the Earth. After a hydrogen bomb explosion, some fall-out is blown into the stratosphere (where there is no weather) and the radioactive particles are often maintained there for several years by air currents before settling on Earth.

One dangerous radioactive isotope in fall-out is strontium-90, with a half-life of 28 years; it is present in the products of nuclear fission (breakdown) of uranium. It can accumulate in bones if it gets into the body and can then induce cancer in the tissues. Since strontium is chemically similar to calcium, strontium-90 can become exchanged for calcium in calcium compounds in the soil.

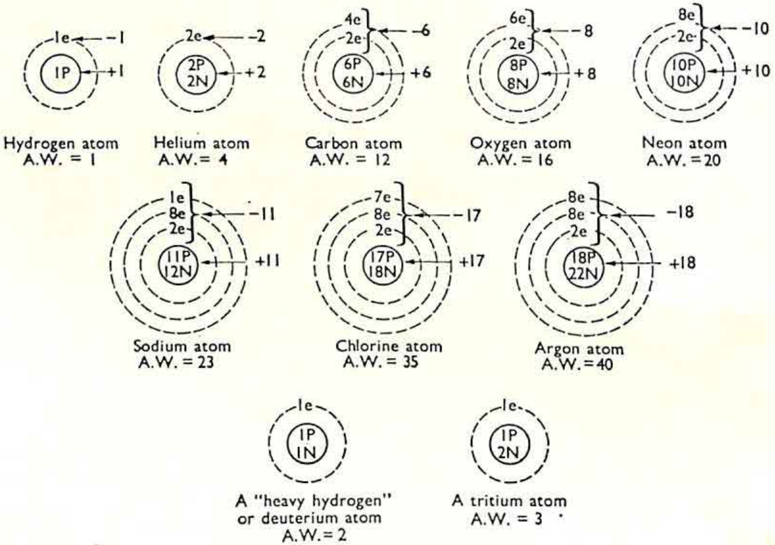
In an atomic bomb, there is a *chain reaction*. When uranium undergoes fission, neutrons are released which then penetrate the nuclei of other uranium atoms so that the whole mass explodes in a very short time.

In an atomic reactor, the rate of fission of uranium is controlled by use of a *moderator* (e.g. graphite).

Radioactive isotopes are often of value as *tracers*. For example, suppose that we wish to know whether or not there is a dynamic equilibrium between a solute (e.g. lead chloride) and its saturated solution. If a radioactive isotope is incorporated into the solute, the radioactivity should be detectable in the saturated solution if there is a dynamic equilibrium.

2.6 ARRANGEMENT OF ELECTRONS IN ATOMS

If the energy levels (shells) around the nucleus are given numbers 1, 2, 3, 4, etc, starting with 1 adjacent to the nucleus, the total number of electrons which can be placed in each level is given by $2n^2$, where n is the number of the level. Hence, level 1 can accommodate 2 electrons, level 2 can accommodate 8, level 3 can accommodate 18, etc.



Hydrogen atom A.W. = 1

Helium atom A.W. = 4

Carbon atom A.W. = 12

Oxygen atom A.W. = 16

Neon atom A.W. = 20

Sodium atom A.W. = 23

Chlorine atom A.W. = 35

Argon atom A.W. = 40

A "heavy hydrogen" or deuterium atom A.W. = 2

A tritium atom A.W. = 3

FIG. 2.6

The electronic arrangements of a few atoms are as follows:

hydrogen 1
helium 2
carbon 2, 4
nitrogen 2, 5
oxygen 2, 6
neon 2, 8
sodium 2, 8, 1
magnesium 2, 8, 2
phosphorus 2, 8, 5
sulphur 2, 8, 6
chlorine 2, 8, 7
argon 2, 8, 8

Apart from helium, all the Rare Gases (neon, argon, krypton, xenon, radon) have eight electrons in their outermost shell.

The diagrammatic representation of some of the above atoms are given in fig. 2.6.

2.7 ATOMIC SYMBOLS

Since all atoms of a particular element are alike, it is possible to represent an atom of any element by a symbol characteristic of that element. The modern symbols were introduced by Berzelius, a few of the most important ones being given in table 2.2.

Table 2.2

Element	*Symbol*	*Element*	*Symbol*	*Element*	*Symbol*
Aluminium	Al	Iodine	I	Platinum	Pt
Barium	Ba	Iron	Fe	Potassium	K
Boron	B	Lead	Pb	Silicon	Si
Bromine	Br	Magnesium	Mg	Silver	Ag
Calcium	Ca	Manganese	Mn	Sodium	Na
Carbon	C	Mercury	Hg	Sulphur	S
Chlorine	Cl	Nitrogen	N	Tin	Sn
Copper	Cu	Oxygen	O	Zinc	Zn
Hydrogen	H	Phosphorus	P		

The symbols are based on the English, Latin or Latinized name of the element. Thus, O represents a single atom of oxygen, 2 O represents two separate atoms of oxygen, 4 N represents four separate atoms of nitrogen, and so on.

Elements do not normally exist as single atoms in the free state, but their molecules contain several atoms. The number of atoms in one molecule of an element is called the *atomicity*. Thus hydrogen, oxygen, nitrogen, chlorine, bromine are diatomic (H_2, O_2, N_2, Cl_2, Br_2), phosphorus vapour is tetratomic (P_4), ozone is triatomic (O_3), sulphur vapour is octatomic (S_8), although the Rare Gases are all monatomic (He, Ne, A (or Ar), Kr, Xe, Rn).

Although elements may have atomicities greater than unity in the solid state, it is customary to write their symbols as though they were monatomic, e.g. sulphur S, iron Fe, etc.

When writing the symbols of isotopes of an element, the mass number is put at the top left-hand corner and the atomic number in the bottom left-hand corner, e.g. ${}^{35}_{17}\mathrm{Cl}$, ${}^{131}_{53}\mathrm{I}$, ${}^{90}_{38}\mathrm{Sr}$, ${}^{1}_{1}\mathrm{H}$.

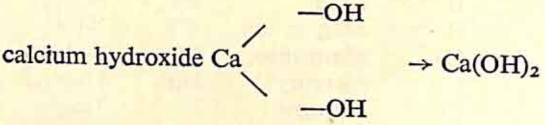
2.8 SIMPLE IDEA OF VALENCY

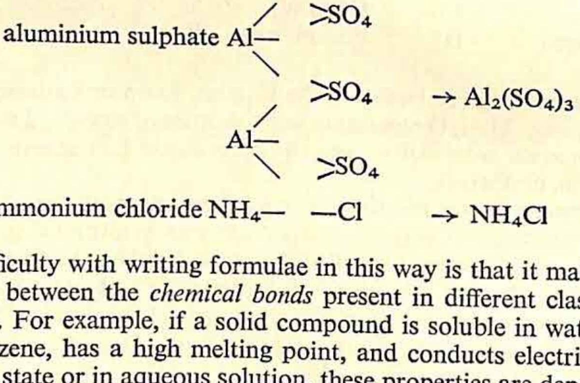
The *valency of an element* is a measure of its combining power with other elements and can be defined as the number of atoms of hydrogen or chlorine combining with one atom of the element. Some elements can have more than one valency, this being termed *variable valency*, e.g. iron (2, 3), copper (1, 2).

Certain groups of atoms, which cannot exist by themselves, are constantly occurring in compounds. They are called radicals, e.g. sulphate SO_4, nitrate NO_3, carbonate CO_3, hydroxide OH, ammonium NH_4.

Table 2.3 gives the valencies of some of the commoner elements and radicals. When writing the formula of a chemical compound, it is only necessary to ensure that all the valency bonds of an element or radical are satisfied.

Examples: sodium chloride Na— —Cl → NaCl





ammonium chloride NH_4— —Cl → NH_4Cl

The difficulty with writing formulae in this way is that it makes no distinction between the *chemical bonds* present in different classes of compound. For example, if a solid compound is soluble in water but not in benzene, has a high melting point, and conducts electricity in the molten state or in aqueous solution, these properties are dependent upon the nature of the valency forces in its structure.

2.9 THE ELECTRONIC THEORY OF VALENCY

The Rare Gases form only a limited number of chemical compounds (although several have been described in recent years, e.g. xenon tetra-

Table 2.3

Valencies of elements and radicals

Monovalent		*Divalent*		*Trivalent*		*Tetravalent*	*Pentavalent*	*Hexavalent*
1		2		3		4	5	6
K	H	Mg	O	Al	N	C	N	S
Na	Cl	Ca	S	Fe (ic)	P	Si	P	
Ag	Br	Ba		Cr		Sn (ic)		
Cu (ous)	I	Zn		PO_4 (phosphate)				
NH_4 (ammonium)		Pb						
OH (hydroxide)		Mn						
NO_3 (nitrate)		Cu (ic)						
NO_2 (nitrite)		Fe (ous)						
OCl (hypochlorite)		Hg						
ClO_3 (chlorate)		Ni						
HCO_3 (bicarbonate)		Sn (ous)						
HSO_4 (bisulphate)		CO_3 (carbonate)						
HSO_3 (bisulphite)		SO_4 (sulphate)						
MnO_4 (permanganate)		SO_3 (sulphite)						
		MnO_4 (manganate)						
		CrO_4 (chromate)						
		Cr_2O_7 (dichromate)						
		SiO_3 (silicate)						

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fluoride XeF_4, xenon hydroxide $Xe(OH)_4$, xenon trioxide XeO_3), and it is therefore assumed that their atoms have *relatively* stable electronic arrangements. Atoms of other elements are assumed to have unstable electronic arrangements and, during the establishment of chemical bonds, it is assumed that a redistribution of electrons occurs so as to leave each atom with the stable electronic configuration of a Rare Gas. In some cases stability is achieved with only the outer electronic configuration of a Rare Gas, but these examples will be left to a more advanced textbook.

Table 2.4

Rare Gas	*Shell*					
	1	2	3	4	5	6
Helium	2					
Neon	2	8				
Argon	2	8	8			
Krypton	2	8	18	8		
Xenon	2	8	18	18	8	
Radon	2	8	18	32	18	8

A stable electronic configuration can be achieved by gain, loss or sharing of electrons.

(a) Ionic valency (electrovalency)

Consider the formation of sodium chloride. If the sodium atom (2, 8, 1) loses an electron, it attains the electronic configuration of neon (2, 8). It has not become neon, however, since it contains one extra proton in its nucleus. It is a charged sodium atom, called a sodium *ion*, and written Na^+. If a chlorine atom (2, 8, 7) gains an electron, it attains the electronic configuration of argon (2, 8, 8). It has not become argon, however, because it contains one less proton in the nucleus. It is a charged chlorine atom, called a chloride *ion*, and written Cl^-. In the formation of sodium chloride, the electron in the outer energy level of the sodium atom (the valency electron) moves over into the outer energy level of the chlorine atom. The two ions formed are held together by electrical attraction (a positive charge attracts a negative charge).

This type of bond is called ionic or electrovalent. A compound like sodium chloride, which contains ionic bonds, exists as ions in the solid state, and there are no atoms or molecules. The ions are arranged in the most stable manner (fig. 2.8) on a *crystal lattice*. When the compound is melted, or dissolved in water, the ions become free to move about and are not confined to a definite pattern as in the solid structure.

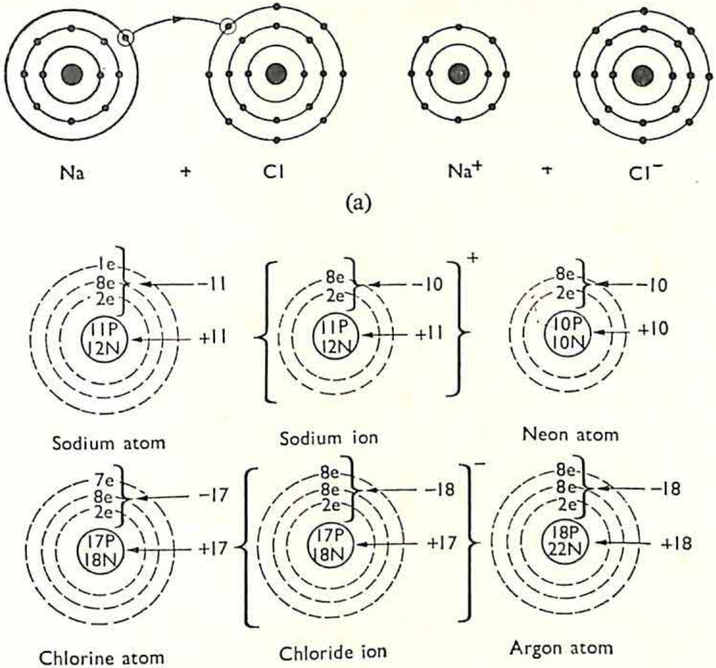


FIG. 2.7

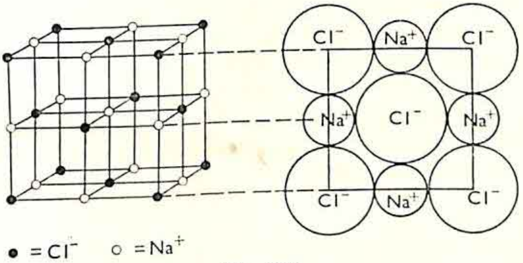


FIG. 2.8

The arrangement of ions in a sodium chloride crystal. The right-hand diagram shows the relative sizes of the sodium and chloride ions. The left-hand diagram shows only the centres of the ions and not their relative sizes

Another example is provided by magnesium chloride.

$$Mg + 2Cl \rightarrow Mg^{++} + 2Cl^{-}$$

Ionic compounds

(*a*) are generally salts, soluble in water,
(*b*) are electrolytes (see 3.1) in the molten state and in aqueous solution,
(*c*) have high melting and boiling points.

It is almost impossible to obtain ions with a charge greater than 3.

(b) Covalency

Here atoms attain a stable electronic configuration by the sharing of electrons between two atoms, each atom providing one electron for the resulting bond. There is no question of an electron transfer in this type of bond.

In hydrogen, for example, each atom provides one electron so that each one attains the stable configuration of helium. Although the electrons are designated differently, this is only to indicate from which atom they come.

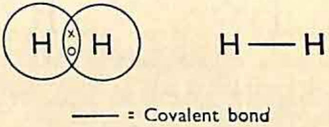


FIG. 2.9

Other examples are shown in fig. 2.10.

Only the outer electronic shells are shown in each case. It is important to realize that covalent compounds contain molecules, although the shapes are not immediately obvious by writing the above electronic formulae. Thus, the molecule of water is not linear. The reasons for this will be left to a more advanced textbook.

Covalent compounds:

(*a*) generally have low melting and boiling points,
(*b*) are non-electrolytes (see 3.1),
(*c*) are either insoluble in water or decomposed by it.

Bonds in Rare Gas compounds, e.g. xenon difluoride, XeF_2, xenon tetrafluoride, XeF_4, xenon trioxide, XeO_3, are covalent rather than ionic, but a more complicated theory must be used to explain their

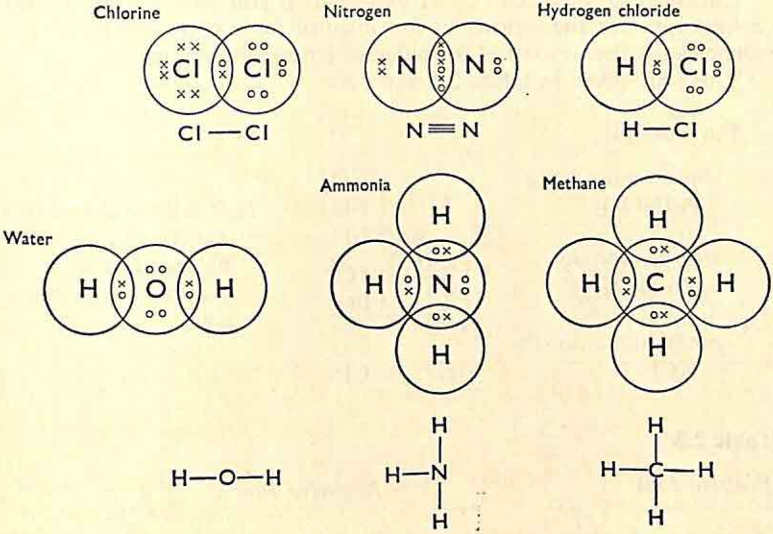
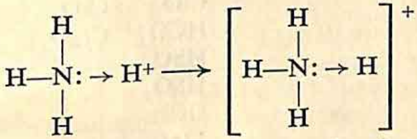


FIG. 2.10

existence than the simple one we have adopted in talking about covalent compounds in this book.

In a special type of covalency called co-ordinate covalency (dative covalency) one atom provides both shared electrons for the covalent bond. An example is provided by the ammonium ion, NH_4^+.

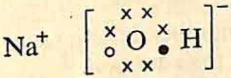


$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{N}}: \rightarrow H^+ \longrightarrow \left[H-\overset{\displaystyle H}{\underset{\displaystyle H}{N}}: \rightarrow H \right]^+$$

$\rightarrow$ = co-ordinate covalent bond

FIG. 2.11

Some compounds contain both electrovalent and covalent bonds, e.g. ammonium chloride $NH_4^+Cl^-$, sodium hydroxide Na^+OH^-.



Na^+ $[O-H]^-$

FIG. 2.12

Chemical formulae can be written easily if you learn (*a*) charges on various ions for the writing of formulae of ionic compounds, (*b*) covalencies for the writing of formulae of covalent compounds.

These are given in tables 2.5 and 2.6.

For example:

aluminium nitrate
$Al(NO_3)_3$ $\qquad Al^{+++}\left\{\begin{matrix}NO_3^-\\NO_3^-\\NO_3^-\end{matrix}\right.$

zinc phosphate
$Zn_3(PO_4)_2$ $\qquad \left\{\begin{matrix}Zn^{++}\\Zn^{++}\\Zn^{++}\end{matrix}\right. \left\{\begin{matrix}PO_4^{---}\\PO_4^{---}\end{matrix}\right.$

potassium chloride
KCl $\qquad K^+ \quad Cl^-$

N.B. All the charges on a given ion must be balanced by a charge of opposite sign.

Table 2.5

Positive Ions				*Negative Ions*		
+	++	+++	++++	−	−−	−−−
H^+	Mg^{++}	Al^{+++}	Sn^{++++}	H^-	O^{--}	N^{---}
Na^+	Ca^{++}	Fe^{+++}		Cl^-	S^{--}	PO_4^{---}
K^+	Ba^{++}	Cr^{+++}		Br^-	CO_3^{--}	
Ag^+	Zn^{++}			I^-	SiO_3^{--}	
Cu^+	Hg^{++}			OH^-	SO_4^{--}	
Hg_2^{2+}	Cu^{++}			NO_3^-	SO_3^{--}	
NH_4^+	Sn^{++}			NO_2^-	MnO_4^{--}	
	Pb^{++}			ClO_3^-	CrO_4^{--}	
	Fe^{++}			HCO_3^-	$Cr_2O_7^{--}$	
	Mn^{++}			HSO_4^-		
	Ni^{++}			HSO_3^-		
				OCl^-		
				MnO_4^-		

What type of bonds do you think exist in sodium bromide, carbon tetrachloride, hydrogen sulphide and potassium chloride?

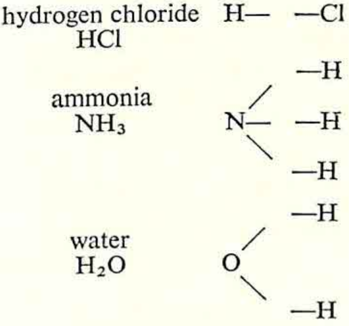
2.10 CHEMICAL EQUATIONS

1. Equations must have the same number of atoms or ions of each element concerned on both sides of the equation.
2. When some or all the reactants and products are ionic compounds,

Table 2.6

Covalencies

1	2	3	4	5	6
H	O	N	C	N	S
Cl	S	P	Si	P	
Br					
I					



an ionic equation should be written. It is important to balance charges on both sides of the equation, for example:

$$AgNO_3 + HCl \rightarrow AgCl\downarrow + HNO_3$$

becomes $Ag^+ + NO_3^- + H^+ + Cl^- \rightarrow AgCl\downarrow + H^+ + NO_3^-$

or $$Ag^+ + Cl^- \rightarrow AgCl\downarrow$$

Another example is:

$$\underset{\text{(NaOH)}}{Na^+ + OH^-} + \underset{\text{(HCl)}}{H^+ + Cl^-} \rightarrow \underset{\text{(NaCl)}}{Na^+ + Cl^-} + H_2O$$

or $$H^+ + OH^- \rightarrow H_2O$$

Another example is:

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2\uparrow$$

or $$Zn + 2H^+ \rightarrow Zn^{++} + H_2\uparrow$$

Another example is:

$$Cl_2 + 2KI \rightarrow 2KCl + I_2$$

or $$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$$

3. Care must be exercised that all formulae of reagents are correctly shown.
4. The equation written must represent a reaction actually taking place.
5. An equation cannot indicate:

(*a*) the physical states of the reactants and products (solids, liquids, gases, solutions, colour, etc); an arrow upwards is used to indicate the formation of a gas and an arrow downwards indicates the formation of a precipitate,

(*b*) whether heat is liberated or absorbed during the reaction, whether heat is needed to start the reaction, the rate of reaction, etc.

If heat is needed, the word 'heat' can be inserted above the arrow, for example:

$$CuCO_3 \xrightarrow{\text{heat}} CuO + CO_2\uparrow$$

Heat liberated or absorbed is indicated after the equation (the symbol used is ΔH, a negative sign indicating heat evolved and a positive sign indicating heat absorbed; thus, when heat is liberated, the system loses heat while the surroundings gain an equivalent amount of heat), for example:

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \qquad \Delta H = -45 \text{ kilocalories}$$

A reversible reaction is indicated by using a double arrow.

2.11 ELECTRONEGATIVITY

Electronegativity is a term used to denote the ability of an atom to attract electrons relative to other atoms. For example, chlorine is highly electronegative since its atoms readily capture an electron forming chloride ions. Other very electronegative elements are oxygen, nitrogen, fluorine and sulphur.

Pauling has devised a scale whereby electronegativities can be given numerical values.

Electropositivity is the opposite of electronegativity. Thus, sodium is highly electropositive (weakly electronegative) since its atoms readily lose an electron forming sodium ions. Other highly electropositive elements are potassium, calcium, magnesium and aluminium.

Notice that metals are generally highly electropositive while non-metals are highly electronegative.

In covalent bonds where two elements of differing electronegativity are participating, the more electronegative element has the greater share in the two electrons of the bond. Thus, in hydrogen chloride, chlorine is the more electronegative and has the greater share of electrons. This is represented as follows:

$$\mathrm{H} \rightarrow\!\!- \mathrm{Cl} \qquad \underset{\text{electrical dipole}}{\overset{+}{\mathrm{H}}\text{—}\overset{-}{\mathrm{Cl}}}$$

There is, however, no question of complete separation of charge, such as occurs in an ionic bond.

Some electronegativities on the Pauling scale are as follows:

			H			
			2·1			
Li	Be	B	C	N	O	F
1·0	1·5	2·0	2·5	3·0	3·5	4·0
Na	Mg	Al	Si	P	S	Cl
0·9	1·2	1·5	1·8	2·1	2·5	3·0
						Br
						2·8
						I
						2·5

2.12 THE PERIODIC TABLE

In 1829, Döbereiner was the first to comment that the second element in the 'triads'

lithium	sodium	potassium
calcium	strontium	barium
sulphur	selenium	tellurium
chlorine	bromine	iodine
iron	cobalt	nickel

had an atomic weight which was almost exactly the arithmetic mean of the first and third elements, e.g. Li = 7, K = 39, Na = 23 (i.e. $(7 + 39) \div 2$). But the differences between different members of the five 'triads' was not uniform—there was hardly any difference at all between Fe, Co, Ni.

Newlands (1863) was the first to see that, if the known elements were written in ascending order of atomic weight, similar properties reappeared in every eighth element, like notes in a musical 'octave'. This system worked well for the lightest elements but, by failing to allow for an expansion of the octave when dealing with heavier elements, the theory broke down.

The first really important system of classification of the elements was devised by the Russian Mendeléeff (1869) when he stated the periodic law; 'the properties of the elements are periodic functions of their atomic weights'. The classification of elements according to their atomic weights produced several anomalies owing to the existence of isotopes (see 2.1, 2.4). For example, cobalt and nickel, argon and potassium, tellurium and iodine come in the wrong order when arranged in order of atomic weight because cobalt, argon and tellurium have a preponderance of isotopes (at that time unrecognized) of high mass number while nickel, potassium and iodine have the reverse.

It has already been seen that the fundamental determinant of properties (especially chemical ones) of the elements is the number of protons (or therefore the number of electrons) in their atoms, the neutrons just giving extra weight to the atoms. In modern classifications, therefore, the elements are arranged in increasing order of ATOMIC NUMBER (see 2.2). A modern Periodic Table (Bohr-Thomsen table) is shown in table 2.7.

You will not, of course, have to remember all the table at this stage of your studies in chemistry, but the whole table has been given so that you can see the general layout. The names of the elements are given at the back of this book, together with their atomic weights.

The use of letters IA, IIA, etc dates from Mendeléeff's table, and it is still a useful method of referring to a particular set of elements. The table is divided into vertical GROUPS and horizontal PERIODS. In the Mendeléeff table there was a necessity for *sub-groups* A and B, which have been abandoned in the modern table. Thus, Mendeléeff had lithium and sodium as the *typical elements* of his Group I, potassium, rubidium and caesium as his A sub-group and copper, silver, gold as his B sub-group. In the modern table, the typical elements have been placed with the sub-group they most resemble. Thus, Group IA contains lithium (Li) to francium (Fr), Group IIA contains beryllium (Be) to radium (Ra), Group VIIB contains fluorine (F) to astatine (At), and so on. The letters A and B are used merely for convenience, and do not imply, for example, that Groups IA and IB are closely related.

Hydrogen is placed at the top of Group IA only because no other satisfactory place can be found for it.

The following points should be remembered:

(*a*) The Group into which an element falls often corresponds to the valency of the element, e.g. sodium is monovalent, magnesium divalent, aluminium trivalent. In other cases, the valency of the element is found by subtracting the number of the Group from 8, e.g. nitrogen is trivalent, oxygen divalent, chlorine monovalent.

The process of 'subtraction from 8' concerns the fact that the

Table 2.7

IA	IIA											IIIB	IVB	VB	VIB	VIIB	O
H 1																	He 2
Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
Na 11	Mg 12	IIIA	IVA	VA	VIA	VIIA	← VIII →			IB	IIB	Al 13	Si 14	P 15	S 16	Cl 17	A 18
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Cs 55	Ba 56	La* 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Fr 87	Ra 88	Ac† 89															
	*Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71			
	†Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lw 103			

* The Lanthanons (Rare Earths).
† The Actinons.
The numbers quoted are atomic numbers.

'hydrogen valency' and 'oxygen valency' of an element must total 8, for example:

Nitrogen ammonia NH_3 nitrogen pentoxide N_2O_5
$V = 3$ $V = 5$
$$\underline{\underline{3 + 5 = 8}}$$

Sulphur hydrogen sulphide H_2S sulphur trioxide SO_3
$V = 2$ $V = 6$
$$\underline{\underline{2 + 6 = 8}}$$

(*b*) Metallic (highly electropositive) elements lie to the left of the table while non-metallic (highly electronegative) elements lie to the right. Elements in the middle of the table are often difficult to classify as metals or non-metals.

(*c*) In passing down a Group, the elements generally become more metallic (electropositive). Thus in Group VB, nitrogen and phosphorus are non-metallic, arsenic and antimony are intermediate between metals and non-metals, while bismuth is a metal.

(*d*) The properties of the elements are normally related in a vertical direction. Thus, fluorine is related to chlorine, bromine, iodine and astatine while lithium is related to sodium, potassium, rubidium, caesium and francium. In some cases, however, there is a horizontal relationship. Thus, the elements in the *transition series* (e.g. scandium (Sc) to zinc (Zn)) are related to one another in a horizontal direction.

Some general chemistry of families of elements

Group IA, the *Alkali Metals*, consists of the family lithium, sodium, potassium, rubidium, caesium, francium (radioactive). It is the most electropositive family in the table. The elements in this family are all soft silvery-white metals which rapidly tarnish in air. They have low melting points (decreasing with increasing atomic number), are malleable and ductile, good conductors of heat and electricity, and have a high lustre. They are the most reactive metals and occupy positions right at the top of the electrochemical series (see 5.1). Their compounds are generally stable and ionic, since the Alkali Metal atoms have one electron in the outer shell which is easily lost to form a stable Rare Gas structure.

$$M \rightarrow M^+ + 1 \text{ electron}$$

Group IIA metals consist of the family beryllium, magnesium, calcium, strontium, barium and radium (radioactive), the last four being called the Alkaline Earths. They are all whitish metals, the Alkaline Earths being rather brittle, with high electrical and thermal conductivities.

They are highly electropositive, being second only to the Alkali Metals as an electropositive family. The lower the metal in the family, the higher its position in the electrochemical series (see 5.1); hence the reactivity of the metals increases in passing down the Group.

$$M \rightarrow M^{++} + 2e$$

The chemistry of beryllium is, in general, different from the rest and the following statements apply only to magnesium and the Alkaline Earths.

Oxides: basic.

Hydroxides: sparingly soluble in water, basic, but weakly so, the strength increasing in passing down the Group.

Salts of strong acids: generally stable, but some salts of magnesium are attacked by water (this is the process called hydrolysis, see 7.11).

Carbonates: evolve carbon dioxide on heating, the ease decreasing in passing down the Group.

Bicarbonates: do not exist out of solution.

Nitrates: give nitrogen dioxide and oxygen on heating, except barium nitrate, which first gives the nitrite.

$$2Ba^{++}(NO_3^-)_2 \rightarrow 2Ba^{++}(NO_2^-)_2 + O_2\uparrow$$

$$\text{strong heat}\quad 2Ba^{++}(NO_3^-)_2 \rightarrow 2Ba^{++}O^{--} + 4NO_2\uparrow + O_2\uparrow$$

In general, the salts become more soluble in passing down the Group, an exception being the sulphates; barium sulphate is one of the most insoluble salts known.

Group IVB contains the elements carbon, silicon, germanium, tin and lead. In passing down the family, the elements become more electropositive, from carbon (typically non-metallic, no salts except where the element is present in the form of a carbonate CO_3^{--} or bicarbonate HCO_3^-), to lead (evidently metallic, *readily* forms salts such as $Pb^{++}SO_4^{--}$, $Pb^{++}(Cl^-)_2$, $Pb^{++}(NO_3^-)_2$). Oxides of carbon and silicon are acidic (although silica SiO_2 is insoluble in water whereas carbon dioxide CO_2 dissolves), while oxides of tin and lead in the tetravalent state (the oxidation state IV, see 4.5) are amphoteric (see 7.9).

In passing down the Group, the tendency to form compounds of the divalent elements increases: tin and lead form stable ions Sn^{++} and Pb^{++}.

Although tin and lead are evidently metallic, they form some tetracovalent compounds, e.g. the unstable hydrides (SnH_4, PbH_4), the tetrachlorides ($SnCl_4$, $PbCl_4$).

Stannous ions are good reducing agents, while plumbous ions are not, this showing that lead is more ready than tin to form the divalent ion.

Group VB contains the elements nitrogen, phosphorus, arsenic, antimony and bismuth. In passing down the family, the electropositive character increases, from nitrogen (gaseous, non-metallic) to bismuth (solid, metallic). The stability of the hydride MH_3 (containing the trivalent element) decreases in passing down the Group; thus, ammonia NH_3 is much more stable than bismuthine BiH_3. After phosphorus, there is a tendency to form compounds in which the element has a trivalency, rather than a pentavalency.

Bismuth alone fairly readily forms salts containing the trivalent cation (Bi^{+++}), e.g. bismuth nitrate $Bi^{+++}(NO_3^-)_3$.

Nitrogen forms many oxides, which are neutral (N_2O, NO) or acidic (N_2O_3, N_2O_4, N_2O_5). Phosphorus forms acidic oxides (P_2O_3, P_2O_5 or P_4O_6, P_4O_{10}—according to structure). Arsenic and antimony form amphoteric oxides. Bismuth forms a basic oxide (Bi_2O_3).

The stability of the trichlorides increases in passing down the Group; nitrogen trichloride is an explosive covalent compound (NCl_3) while bismuth trichloride is stable and ionic ($Bi^{+++}(Cl^-)_3$).

Transition elements

These have several notable general features:

(*a*) They exhibit variable valency (i.e. can exist in a variety of oxidation states, see 4.5), e.g. iron shows main valencies of 2 and 3, chromium of 3 and 6, etc.

(*b*) They often form coloured ions in aqueous solution, e.g. ferrous ions (green), ferric ions (yellow), cupric ions (blue).

(*c*) They readily form complex ions (see 6.8), e.g. cuprammonium ions $[Cu(NH_3)_4]^{++}$ (deep blue).

(*d*) Many of the metals and their salts often have high catalytic activity (see 16.4), e.g. nickel is used in hydrogenation reactions (see 6.5).

The *Halogens* (the word means 'salt producer') consist of the family fluorine, chlorine, bromine, iodine and astatine (radioactive). It is the most electronegative family in the table. Fluorine and chlorine are pale green gases at normal temperatures, bromine is a red-brown liquid, and iodine a black solid. They have one electron less than the structure of a Rare Gas and therefore form negative ions very easily, as in sodium chloride Na^+Cl^-.

$$X + 1 \text{ electron} \rightarrow X^-$$

With other electronegative elements, the Halogens form compounds containing covalent bonds, e.g. hydrogen chloride HCl, phosphorus trichloride PCl_3.

Halogens are oxidizing agents (see 4.1), the strength decreasing in passing down the series. Since their ability to act as oxidizing agents depends upon their ability to remove electrons from other atoms or ions, it might be expected that their strength as oxidizing agents would decrease as the size of their atoms gets larger (the electrons removed would be closer to the attraction of the nucleus for a smaller Halogen atom); the atomic size increases with increasing atomic number.

2.13 ATOMIC RADII

The radius of an atom is the distance measured from the centre of the nucleus to the extreme shell of electrons around the nucleus.

The atomic radius determines the electronegativity of an element. Thus, the radius of the sodium atom is larger than that of iron, making the valency electron of sodium more easily removed, i.e. sodium is the more electropositive. There is a whole philosophy of chemistry based on atomic radii. For example, the fact that the atomic radius of sodium is larger than that of iron makes the former softer (the atom can be compressed more easily), a better thermal and electrical conductor (the valency electron is further from the attraction of the nucleus), and lighter (the volume of the atom is very large, density being mass per unit volume).

2.14 METALLIC STRUCTURES

Metals have structures in which the atoms are 'close-packed', the number of neighbours surrounding a given atom being normally twelve (but sometimes eight). The structures contain positively charged ions together with a cloud of electrons which can move freely throughout the structure. It is this cloud which gives the metal its characteristic properties such as electrical conductivity.

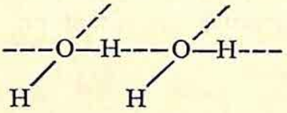
2.15 VAN DER WAALS' BONDS

In some structures, e.g. graphite, there are weak forces (van der Waals' forces) holding the atoms or molecules together. These forces arise owing to the attraction of atomic or molecular dipoles (see 2.11).

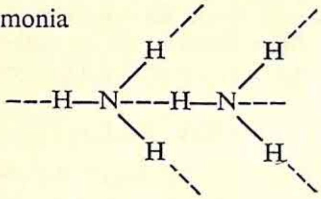
2.16 HYDROGEN BONDS

In compounds containing hydrogen atoms together with atoms of a highly electronegative element (nitrogen, oxygen, fluorine), the hydrogen atoms can act as a 'bridge' between atoms of the electronegative element forming a 'hydrogen bond'. Examples are water H_2O and ammonia NH_3. Since the boiling point of a molecular liquid depends, to a large extent, on its molecular weight (see 2.17), the boiling points of liquids like water and ammonia are higher than expected since hydrogen bonding effectively increases the molecular weight.

water



ammonia



2.17 MOLECULAR WEIGHTS

The molecular weight of an element or compound is defined as the weight of one molecule of it compared with the weight of one atom of a standard element, the most recent standard being carbon (C = 12).

$$\text{M.W.} = \frac{\text{Wt of 1 molecule of element or compound}}{\frac{1}{12} \times \text{wt of 1 atom of carbon}}$$

To calculate molecular weights, or formula weights of ionic compounds, the atomic weights are added up.

Examples:

1. sodium carbonate Na_2CO_3 (an ionic compound)

$$\text{Na} = 23, \text{C} = 12, \text{O} = 16$$

$$\text{Formula wt} = 2 \times 23 + 12 + 3 \times 16 = 106$$

2. benzene C_6H_6 (a covalent compound)

$$\text{C} = 12, \text{H} = 1$$

$$\text{Molecular wt} = 6 \times 12 + 6 \times 1 = 78$$

2.18 PERCENTAGE COMPOSITION FROM FORMULA

Examples:

1. Find the percentage of oxygen in water, H_2O

$$H = 1, O = 16, \text{M.W.} = 2 + 16 = 18$$

$$\text{Fraction of oxygen per molecule} = \frac{16}{18}$$

$$\text{\% of oxygen per molecule} = \frac{16 \times 100}{18} = 88{\cdot}89\%$$

2. Find the percentage by weight of water in sodium carbonate decahydrate.

Many salts crystallize with molecules of water attached to them, and sodium carbonate is an example, the formula of its hydrate being $Na_2CO_3.10H_2O$.

$$Na = 23, C = 12, O = 16, H = 1$$

$$\text{Formula weight} = 2 \times 23 + 12 + 3 \times 16 + 10(2 + 16) = 286$$

$$\text{\% of water per formula weight} = \frac{180 \times 100}{286} = 62{\cdot}9\%$$

2.19 CALCULATIONS FROM EQUATIONS

A chemical equation can give many quantitative details about a reaction.

Examples

1. Find the weight of hydrogen produced when 6·55 g of zinc are reacted with excess dilute sulphuric acid.

$$Zn = 65{\cdot}5, H = 1\ (S = 32, O = 16)$$
$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2\uparrow \quad (\text{or } Zn + 2H^+ \rightarrow Zn^{++} + H_2\uparrow)$$

The equation tells us that the atomic weight (in units of weight) of zinc reacts with sulphuric acid (it is assumed that more than enough is available to react with the given amount of metal, i.e. an excess) to give the formula weight (in units of weight) of zinc sulphate (or one zinc ion, in units of weight) plus the molecular weight (in units of weight) of hydrogen.

Hence, 65·5 g of zinc react with excess acid to give 161·5 g of zinc sulphate and 2 g of hydrogen. That is:

$$65{\cdot}5 \text{ g of zinc} \rightarrow 2 \text{ g of hydrogen}$$
$$\therefore \quad 1 \text{ g of zinc} \rightarrow \tfrac{2}{65} \text{ g of hydrogen}$$
$$\therefore \quad 6{\cdot}55 \text{ g of zinc} \rightarrow \frac{2 \times 6{\cdot}55}{65{\cdot}5} = \underline{0{\cdot}2 \text{ g}} \text{ of hydrogen}$$

2. What weight of oxygen could be obtained by heating 490 g of potassium chlorate?

$$\mathrm{K} = 39,\ \mathrm{Cl} = 35{\cdot}5,\ \mathrm{O} = 16$$
$$2\mathrm{KClO_3} \rightarrow 2\mathrm{KCl} + 3\mathrm{O_2}\uparrow$$
$$\begin{array}{rl} 2(39 + 35{\cdot}5 + 48) \text{ g} \rightarrow & 3(2 \times 16) \text{ g} \\ 245 \text{ g} \rightarrow & 96 \text{ g} \\ \therefore \quad 490 \text{ g} \rightarrow & 2 \times 96 = \underline{192 \text{ g}} \text{ of oxygen} \end{array}$$

N.B. Generally, *volumes* of gases (rather than weights) are required (see 2.20).

2.20 CONVERSIONS OF WEIGHTS OF GASES TO VOLUMES

The molecular weight has no units, although it is often convenient to express it in grams when it is called the *gram molecular weight*.

Gas	*M.W.*	*1 G.M.W. equals*
Oxygen, O_2	32	32 grams
Hydrogen chloride, HCl	36·5	36·5 grams
Nitric oxide, NO	30	30 grams

The gram molecular weight of any gas contains a fixed number of molecules, called the Avogadro number ($N = 6 \times 10^{23}$). Suppose that the absolute weight of the carbon atom is m. Then

$$\text{M.W. of gas or vapour} = \frac{\text{Wt of 1 molecule of gas or vapour}}{\frac{1}{12} \times m}$$

or $$\text{Wt of 1 molecule of gas or vapour} = M \times m/12$$

Thus, for oxygen, Wt of 1 molecule $= 32 \times m/12$

i.e. $$\text{number of molecules per gram molecule} = \frac{32 \times 12}{32 \times m} = \frac{12}{m}$$

This is also true for all other gases, the quantity $12/m$ being the Avogadro number.

Avogadro's hypothesis (2.1) tells us that equal volumes of all gases under the same conditions of temperature and pressure contain equal numbers of molecules. If the gram molecular weight of any gas contains a fixed number of molecules, therefore, it must occupy a definite volume at a fixed temperature and pressure. That chosen is normal temperature (0°C, 273°Å) and normal pressure (760 mm of Hg), i.e. *N.T.P.* It is found that 1 gram-molecule of any gas at N.T.P. occupies a volume of 22·4 litres. This is called the *gram molecular volume.*

Example: In example (1) given in 2.19, find what volume of hydrogen is evolved at N.T.P.

2 g of hydrogen occupy 22,400 cm³ at N.T.P.

$$\therefore \quad 0{\cdot}2 \text{ g of hydrogen occupy } \frac{22{,}400 \times 0{\cdot}2}{2} = 2{,}240 \text{ cm}^3$$

The volume of gas should, for preference, be obtained *directly*:

$$65{\cdot}5 \text{ g of Zn} \rightarrow 22{,}400 \text{ cm}^3 \text{ of } H_2 \text{ at N.T.P.}$$
$$\therefore \quad 6{\cdot}55 \text{ g of Zn} \rightarrow \underline{2{,}240 \text{ cm}^3}$$

2.21 USE OF THE GENERAL GAS EQUATION

Boyle's law states that the volume of a given mass of dry gas varies inversely as the pressure to which it is subjected at constant temperature.

$$P \, \alpha \, 1/V \text{ or } PV = k, \text{ where k is a constant}$$

Charles's law states that a gas expands by $\frac{1}{273}$ of its volume at 0°C for every degree rise in temperature (at constant pressure). This can be shown to be equal to the statement that the volume of a gas is directly proportional to its absolute temperature at constant pressure.

$$V \propto T$$

By combination of these two laws, the general gas equation can be deduced. If P = pressure, V = volume and T = absolute temperature:

$$\frac{P_1 \times V_1}{T_1} = \frac{P_2 \times V_2}{T_2}$$

Example: Find the volume occupied by 200 cm³ of dry air at 15°C and 760 mm of Hg when its conditions are altered to 0°C and 760 mm.

N.B. 0°C + 273 = °A.

Applying the general gas equation:

$$\frac{760 \times V_1}{273} = \frac{760 \times 200}{(273 + 15)}$$

where V_1 is the required volume

$$V_1 = \frac{200 \times 273}{288} = \underline{189{\cdot}5 \text{ cm}^3}$$

2.22 VAPOUR DENSITY

The vapour density of a gas is the weight of a certain volume of the gas (or vapour) divided by the weight of an equal volume of a standard gas (normally hydrogen), under the same conditions of temperature and pressure.

The vapour density is half the molecular weight.

$$\text{V.D.} = \frac{\text{Wt of 1 volume of gas or vapour}}{\text{Wt of equal volume of hydrogen (same conditions)}}$$

By Avogadro's hypothesis

$$\text{V.D.} = \frac{\text{Wt of 1 molecule of gas or vapour}}{\text{Wt of 1 molecule of hydrogen}}$$

Assuming that hydrogen is H_2

$$\text{V.D.} = \frac{\text{Wt of 1 molecule of gas or vapour}}{2 \times \text{Wt of 1 atom of hydrogen}}$$

$$\therefore \; \underline{2 \times \text{V.D.} = \text{M.W. of gas or vapour}} \text{ (on hydrogen scale)}$$

2.23 GRAHAM'S LAW OF DIFFUSION

Diffusion is the slow passage of one substance into another when they are placed together. Graham stated that the relative rate of effusion (proportional to diffusion) of two gases through a porous plug is inversely proportional to the square roots of their densities.

$$\frac{r_1}{r_2} = \sqrt{\frac{D_2}{D_1}} = \sqrt{\frac{M_2}{M_1}}$$

(r = rate, D = density, M = molecular weight)

Hence, the larger the molecular weight of a gas, the slower its rate of effusion (diffusion).

If the times taken by equal volumes of the gases to effuse are t_A and t_B,

$$\frac{t_A}{t_B} = \sqrt{\frac{M_A}{M_B}}$$

2.24 THE KINETIC THEORY OF GASES

This theory is able to account for the properties of gases as expressed by the gas laws, e.g. Boyle's law, Charles's law, Graham's law, Avogadro's hypothesis.

It is supposed that a gas contains small molecules which are in continual rapid motion in every direction. These molecules are perfectly elastic spheres which are constantly colliding with each other and with the walls of the vessel containing the gas. The motion of the molecules increases as the temperature of the gas is raised since increase of temperature increases the energy of the system.

The pressure exerted by a gas is supposed, on this theory, to result from the collective force of the impacts of the moving molecules on the walls of the container holding the gas. The walls are, in effect, constantly being bombarded. The collisions between the molecules, and between the molecules and the walls, will increase in number as the volume of the container is decreased, for there is then less room for motion. It is this increase in the number of collisions which accounts for the relation between a decrease in volume and an increase in pressure (Boyle's law).

In hydrogen at N.T.P., the average velocity of the molecules is 183,800 cm per second (about 1 mile per second) and, on an average, each molecule travels 0·0000178 cm before colliding with another. This means that each molecule undergoes $\frac{183,800}{0{\cdot}0000178}$, or 10,330,000,000 collisions per second!

It should be remembered that the molecules, atoms or ions in a liquid are also in constant rapid motion (kinetic theory of liquids).

2.25 QUESTIONS

1. What volume of oxygen at N.T.P. is evolved when 24·5 g of potassium chlorate are heated? [6·72 l]
2. What volume of hydrogen at 20°C and 750 mm of Hg is evolved when 6·55 g of zinc are reacted with excess dilute sulphuric acid? [2·43 l]

3. A sample of dry air occupies 200 cm^3 at N.T.P. What volume will it occupy at 27°C and 755 mm of Hg pressure? [218·3 cm^3]
4. Find the percentage by weight of water in cupric sulphate pentahydrate $CuSO_4.5H_2O$ (Cu = 63·5, S = 32, O = 16, H = 1), and the percentage by weight of nitrogen in ammonium sulphate $(NH_4)_2SO_4$ (N = 14). [36·2%, 21·2%]
5. Write formulae for cupric hydroxide, aluminium chloride, calcium nitrate, zinc carbonate and sodium sulphate.
6. A gas has a volume of 300 cm^3 at 27°C and 380 mm. Calculate its volume at N.T.P. [136·5 cm^3]
7. A gas has a volume of 200 cm^3 at 27°C and 760 mm. Calculate the volume of gas at (*a*) 327°C and 760 mm, (*b*) −123°C and 380 mm. [(*a*) 400 cm^3, (*b*) 200 cm^3]
8. Calculate the normal density of carbon dioxide, given that 1·63 g of it occupies a volume of 890 cm^3 at 748 mm. [1·963 g/l]
9. The two chlorides of tin contain respectively 62·6% and 45·5% of the metal by weight. Show that these figures are in agreement with the Law of Multiple Proportions.
10. Two oxides of a metal contain respectively 22·2% and 30·0% by weight of oxygen. Show that these figures illustrate the Law of Multiple Proportions.
11. A salt forms two crystalline compounds with water, the compositions being as follows:

	1	2
Anhydrous salt	63·86	89·83
Water	36·14	10·17

Show that these figures illustrate the Law of Multiple Proportions.

12. An element X has valencies of 2 and 3. Write the simplest formulae for the sulphates, nitrates and oxides of X.
13. Calculate the percentage by weight of iron in ferric sulphate, $Fe_2(SO_4)_3$. [28%]
14. Calculate the percentage by weight of nitrogen in calcium cyanamide, CaNCN. [35%]
15. Zinc nitrate crystals contain 36·36% by weight of water of crystallization. What is the formula of the crystals? [$Zn(NO_3)_2.6H_2O$]
16. Find the volume of carbon dioxide, measured at 13°C and 770 mm, which is liberated by the action of heat on 4·41 g of sodium bicarbonate. [608 cm^3]
17. Find the volume of ammonia at N.T.P. which is liberated when 3·3 g of ammonium sulphate are warmed with sodium hydroxide solution. [1·12 l]

18. 5·0 g of a mixture of cupric oxide and copper produced 4·3 g of copper on reduction with hydrogen. Given that the cupric oxide contains 80% by weight of copper, find the composition of the original mixture. [30% Cu]

2.26 HISTORICAL DEVELOPMENT

The historical development of the ideas of atoms and molecules may be summarized as follows:

1774. Lavoisier. Law of Conservation of Mass. 1799. Proust. Law of Constant Composition. 1803. Dalton. Law of Multiple Proportions. 1792. Richter. Law of Equivalents.	led up to	Dalton's Atomic Theory	gave the idea of	An atom of an element. A compound atom (now called a molecule) of a compound.
1808. Gay-Lussac's Law.	led up to	Avogadro's Hypothesis	gave the idea of	Molecules of an element.

2.27 DEFINITIONS

It is very important to realize that there is no such thing as an atom of a compound. An atom of an element, and a molecule of an element or compound may be defined as follows:

An atom of an element is the smallest uncharged particle of an element which can **possibly** *be obtained.*

Alternatively, *an atom of an element is the smallest uncharged particle of the element which can take part in a chemical change.*

A molecule of an element is the smallest particle of the element that can exist by itself **under ordinary conditions** (*or in the free state*).

The atomicity of an element is the number of atoms contained in 1 *molecule of the element.*

A molecule of a compound is the smallest particle of the compound that can exist by itself **under ordinary conditions** (*or in the free state*).

A molecule of a compound must contain at least two different atoms; otherwise it would not be a compound, but an element. This enables us to define

an element as a substance containing only one kind of atom, and

a compound as a substance containing at least two different kinds of atoms combined together.

2.29 FORMULAE

If it is known that a particular compound exists and the valencies of its component atoms or radicals are known then it is possible to write down its correct formula. It is, therefore, very important to learn the valencies listed in section 2.8.

The following points will be helpful,

(*a*) Most common metals have a valency of 2. Exceptions are potassium, sodium, silver and cuprous copper (1), aluminium and ferric iron (3).

(*b*) Remembering any formulae involving hydrogen atoms enables valencies to be derived. For instance, if you can remember that the formula of sulphuric acid is H_2SO_4 then it follows from the definition of valency (see 2.8) that the valency of the sulphate radical is 2. Similarly the formula HCl shows the valency of chlorine to be 1, and the formula H_2O gives the valency of oxygen as 2 or of the hydroxide radical as 1.

(*c*) One word of warning is necessary. A compound does not exist simply because a formula can be written for it.

2.30 USES OF AVOGADRO'S HYPOTHESIS*

The simple uses of Avogadro's hypothesis may be summarized as follows:

(*a*) It introduces the idea of a molecule of an element (see 2.1), or, in other words, the idea of the atomicity of an element (see 2.1).

(*b*) It accounts for Gay-Lussac's law (see 2.1).

(*c*) It enables the molecular formulae of gases to be found, e.g. hydrogen is diatomic, H_2 (see 2.1).

(*d*) It leads to the important relationship M.W. = 2 × V.D. This provides one of the main methods of obtaining molecular weight values by first measuring vapour densities (see 2.22).

(*e*) It leads to the ideas of gram molecular weight and gram molecular volume, and the important result that 1 gram molecular weight of any gas occupies 22·4 litres at N.T.P. This result enables a weight of a gas to be converted into a volume and vice versa (see 2.20).

(*f*) It leads to Cannizzaro's method of determining atomic weights (see 15.5).

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* An hypothesis is something put forward to explain some scientific observations. A law is a concise statement summarizing many separate experimental results all leading to the same conclusion.

3 Electrolysis

3.1 DEFINITIONS

An *electrolyte* is a substance which, in the molten state or in aqueous solution, will conduct an electric current.

Electrolytes can be *strong* or *weak* according to whether they produce a large number of ions or a small number of ions in the molten state or in solution. The electric current is carried by the ions of the electrolyte, i.e. carried through the solution or liquid by the ions into which the electrolyte divides (dissociates) (cf. a current carried along a wire by electrons) and electrolytic conduction therefore provides direct evidence for the existence of ions. Strong electrolytes include all salts (e.g. Na^+Cl^-, $Cu^{++}SO_4^{--}$), strong alkalis (e.g. Na^+OH^-, K^+OH^-) and strong acids in aqueous solution (e.g. H_2SO_4, HCl, HNO_3). Weak electrolytes include weak organic acids such as acetic acid, citric acid, oxalic acid and weak alkalis (e.g. ammonia solution).

Water is a weak electrolyte.

In solutions of weak electrolytes, there are both molecules and ions in equilibrium, for example:

$$H_2O \rightleftharpoons H^+ + OH^-$$
$$\underset{\text{acetic acid}}{CH_3COOH} \rightleftharpoons H^+ + \underset{\text{acetate ions}}{CH_3COO^-}$$

The double arrow indicates that ionization is incomplete. In any given solution of a weak electrolyte there is a constant relationship between the number of molecules and the number of ions present. If any ions are removed from the solution, more molecules immediately ionize to restore balance, this being deduced by application of Le Chatelier's principle (see 8.8).

Non-electrolytes are substances which, in the molten state or in aqueous solution, will not conduct an electric current. Examples include glucose, ethyl alcohol, petrol, oils, i.e. covalent compounds.

The ability of electrolytes to conduct a current can be demonstrated with the apparatus of fig. 3.1.

By increasing the voltage stepwise from about 1·5 to 9 volts, and recording the voltage needed to make the bulb glow, it is possible to make a rough comparison of the ease with which electricity passes through different substances. (Between experiments, the apparatus is washed out thoroughly with distilled water, then acetone, and dried.)

Original substance	*Addition*	*Glow from bulb*
1. Sodium chloride (dry)	—	None
2. Sodium chloride (dry)	Moistened with distilled water	Bright
3. Pure water (i.e. distilled or deionized)	—	None
4. Tap water (contains ions, see 2.9)	—	Bright
5. Pure acetone	—	None
6. Pure ethanol	—	None
7. Pure water	Bench dil. hydrochloric acid	Bright
8. Pure water	Bench dil. sodium hydroxide solution	Bright
9. Pure water	Cupric sulphate solution	Bright
10. Pure water	Ferric chloride solution	Bright
11. Pure water	Sucrose or glucose solution	None
12. Pure water	Suspension of barium sulphate	None

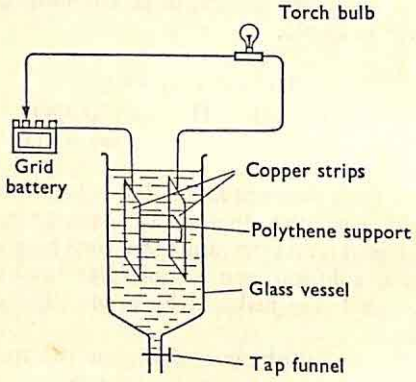


FIG. 3.1

13. Pure glacial acetic acid does not conduct, but the bulb lights up when the acid is diluted with distilled water, being dim at first and getting brighter with dilution. This shows that the degree to which the acid is ionized depends on the dilution, and is greater the greater the dilution.

14. A molten salt, e.g. lead bromide $Pb^{++}(Br^{-})_2$, potassium iodide $K^{+}I^{-}$, will cause the bulb to light up. The salt is contained in a

porcelain crucible, instead of the glass vessel shown in fig. 3.1. Both these salts melt easily.

15. A molten organic compound (see chapter 10), e.g. naphthalene, polythene, will not conduct electricity.

Electrolysis is the sorting and sifting of the ions in an electrolyte and their release (often as visible materials) at the *electrodes* (the points at which the current enters and leaves the solution). The electrode at which the current enters is called the *anode* while that at which it leaves is the *cathode*.

An apparatus in which electrolysis is conducted is called a *voltameter*. Direct current must be employed, and not alternating current, the normal source being a battery or a direct current dynamo. It is convenient to consider this as a pump for electrons. When a current is passed through the solution, positive ions migrate to the cathode (negative electrode) and are called *cations*. Negative ions migrate to the anode (positive electrode) and are called *anions*. When an ion reaches its electrode, its charge is neutralized either by taking electrons from the electrode (cations take electrons from the cathode, which has an excess of electrons) or by giving up electrons to the electrode (anions give up electrons to the anode, which is deficient in electrons).

Voltameters for use when gases are collected

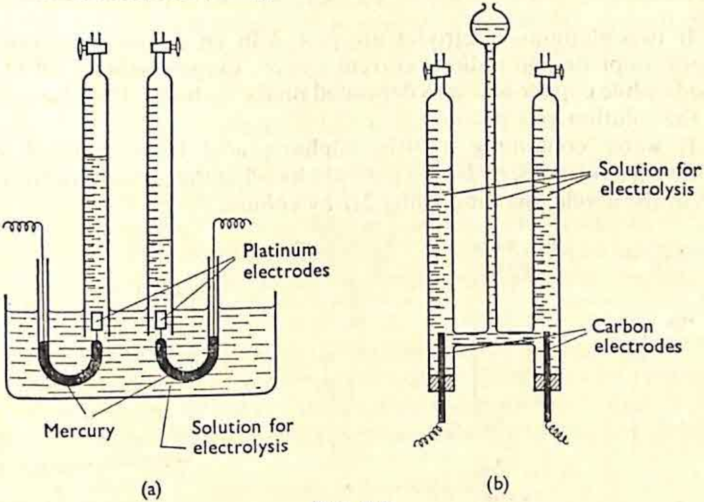
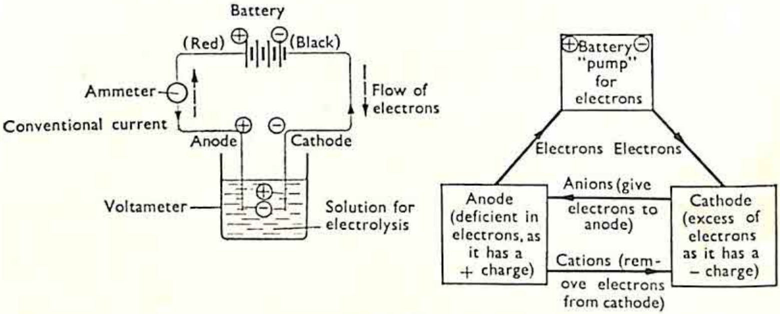


FIG. 3.2

It is important in electrolysis to specify the nature of the electrodes, since secondary reactions can occur between the electrodes and substances liberated there, and also the temperature and concentration of the electrolyte, etc.



Terms used in electrolysis

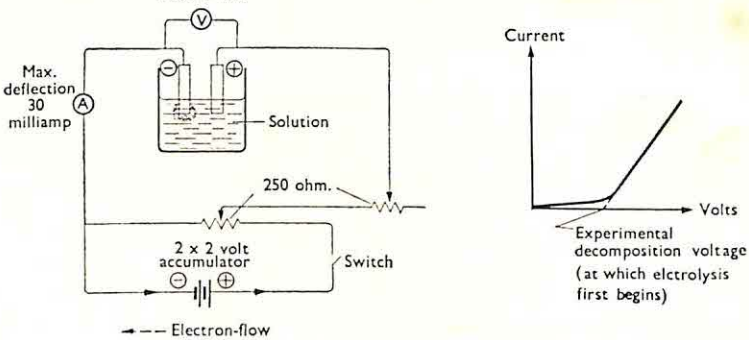
Mechanism of electrolysis

Battery
(Red) ⊕
⊖ (Black)
Ammeter
Conventional current
Flow of electrons
Anode
Cathode
Voltameter
Solution for electrolysis
⊕ Battery ⊖ "pump" for electrons
Electrons
Electrons
Anode (deficient in electrons, as it has a + charge)
Anions (give electrons to anode)
Cations (remove electrons from cathode)
Cathode (excess of electrons as it has a − charge)

FIG. 3.3

If two platinum electrodes are placed in an aqueous solution of cupric sulphate and a direct current passed, oxygen bubbles off at the anode while copper becomes deposited on the cathode. The blue colour of the solution gets paler.

If water containing a little sulphuric acid is electrolysed with platinum electrodes, hydrogen gas bubbles off at the cathode and oxygen gas at the anode, the ratio being 2:1 by volume.



Max. 4 volt
V
Max. deflection 30 milliamp
A
Solution
250 ohm.
2 x 2 volt accumulator
Switch
Electron-flow
Current
Volts
Experimental decomposition voltage (at which elctrolysis first begins)

FIG. 3.4

Fig. 3.4 shows a typical arrangement for investigating the variation of current with applied voltage. By altering the setting of the variable resistance the voltage across the cell can be varied between a negligible value and about 4 volts.

3.2 FARADAY'S LAWS

1. The weight of substance liberated at an electrode is directly proportional to the quantity of electricity passed.

Quantity of electricity is measured in *coulombs*, 1 coulomb being the quantity passing when 1 ampere flows for 1 second, i.e.

Number of coulombs = Number of amperes × Number of seconds

In symbols, $M = e \times i \times t$

where M = mass, i = current, t = time in seconds, e = a constant called the *electrochemical equivalent* of the substance (i.e. the number of grams of substance deposited by the passage of 1 coulomb), e.g. the e.c.e. of silver is 0·001118, while that of hydrogen is 0·00001044.

2. When the same current is passed through a series of electrolytes for a definite time, the weights of substances liberated at the electrodes are in the ratio of their chemical equivalent weights (see 15.1).

$$\frac{\text{Wt of substance A liberated}}{\text{Wt of substance B liberated}} = \frac{\text{E.Wt of A}}{\text{E.Wt of B}}$$

96,540 coulombs (1 faraday) of electricity will liberate the equivalent weight in grams of any element. If the weight of an element liberated by a known quantity of electricity is measured in a voltameter, the weight which would be liberated by 96,540 coulombs can be calculated. Hence, chemical equivalents can be determined by use of the second law of electrolysis.

Example: What weight of silver is deposited from a solution of silver nitrate by a current of 0·075 amp. flowing for 17 minutes? Given also that the equivalent weights of copper and silver are 31·75 and 107·88 respectively, what weight of copper is deposited by the same quantity of electricity?

$$\text{e.c.e. of silver} = 0{\cdot}001118$$

$$\text{Wt of silver} = 0{\cdot}001118 \times 0{\cdot}075 \times 17 \times 60 = \underline{0{\cdot}0856\text{ g}}$$

Also

$$\frac{\text{Wt of copper deposited}}{0{\cdot}0856} = \frac{31{\cdot}75}{107{\cdot}88}$$

$$\therefore \quad \text{Wt of copper deposited} = \frac{0{\cdot}0856 \times 31{\cdot}75}{107{\cdot}88} = \underline{0{\cdot}0252\text{ g}}$$

3.3 SELECTIVE DISCHARGE

At the cathode there is usually a transfer of electrons to a cation to give a neutral atom, i.e. the cathodic process is *reduction* (see 4.1) since electrons are *added* to the ion, for example:

$$Na^+ + 1 \text{ electron} \rightarrow Na$$

The electrochemical series (see 5.1) lists the metals in decreasing order of their reducing power, i.e. in decreasing order of their ability to form cations. This is clearly the order of increasing ease of discharge of the ions.

If only one cation is present in the vicinity of the cathode it will be discharged but, if two or more cations are present, one will be discharged more easily than the others. This is called *selective discharge*. If a solution containing Na^+, H^+ and Cu^{++} ions is electrolysed, the Cu^{++} ions will normally be discharged first at the cathode since they are the most readily reduced back to atoms. Once all the Cu^{++} ions have been discharged, H^+ ions will be discharged and then Na^+ ion.

At the anode there is a loss of electrons by an anion to give a neutral atom or radical. The anodic process is therefore an *oxidation* (see 4.1) since electrons are *removed* from an ion, for example:

$$Cl^- - 1 \text{ electron} \rightarrow Cl$$

If two or more anions are present in the vicinity of the anode, one will be selectively discharged. For example, if sulphate and hydroxide ions are present, the hydroxide ions will be discharged first.

There are sometimes cases when the simple idea of selective discharge does not work. *At the cathode*, if a cation A is in much higher concentration than another cation B, then A may be discharged in preference to B even though the order in the series would predict otherwise.

In some cases an ion is not discharged as easily as its order in the series would predict, e.g. the discharge of H^+ ions at a mercury cathode. This is called the *overvoltage* effect. *At the anode*, there are three possibilities:

(*a*) Straightforward discharge of an anion.

(*b*) In high concentration an anion B may be discharged in preference to another anion A, even though the position in the series predicts otherwise; there can also be an overvoltage effect, e.g. OH^- ions at a lead anode.

Table 3.1

The selective discharge of ions

K^+	↓ increasing ease of discharge at the cathode, i.e. increasing ease of reduction to atoms
Na^+	
Ca^{++}	
Mg^{++}	
Al^{+++}	
Zn^{++}	
Fe^{++}	
Sn^{++}	
Pb^{++}	↑ increasing ease of discharge at the anode, i.e. increasing ease of oxidation to atom or radical
H^+	
Cu^{++}	
OH^-	
Ag^+	
Cl^-	
NO_3^-	
SO_4^{--}	

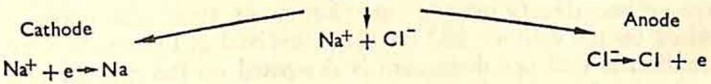
(*c*) It may be easier for the electrode material to ionize. Thus, using a copper anode, the process

$$Cu - 2e \rightarrow Cu^{++}$$

will take place provided it is easier for it to do so than the normal discharge of an anion.

3.4 EXAMPLES OF ELECTROLYSIS

(a) Molten sodium chloride, carbon electrodes



Industrially, this is used in the Downs cell for the manufacture of sodium. The electrolyte is sodium chloride plus about 60 per cent calcium chloride (to lower the melting point) at 580°C.

Electrolysis of fused lead bromide

Place a small quantity of the salt in an evaporating basin or a boiling tube and warm it gently until it melts (380°C). Place iron and graphite electrodes in the melt and adjust the variable resistance (fig. 3.5) until a current of about 3 amp. is flowing. Notice that, after a time, bromine is evolved at the positive electrode while lead is deposited on the negative one. The lead bromide deposited on the lead can be removed and the metal shown to mark paper.

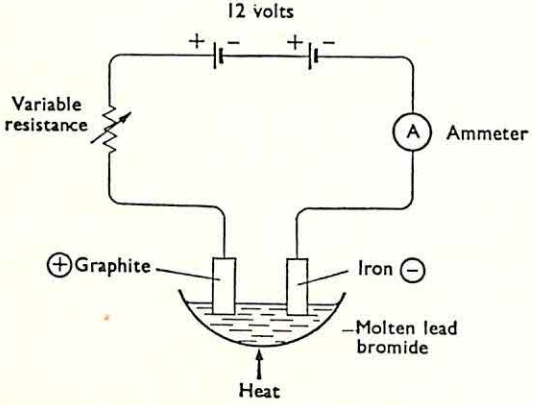


FIG. 3.5

(b) Other important examples of electrolysis of molten salts

Electrolysis of molten magnesium chloride is used to manufacture magnesium, molten calcium chloride (plus a little calcium fluoride) to manufacture calcium, and pure aluminium oxide dissolved in molten Cryolite Na_3AlF_6 to manufacture aluminium. Here, aluminium is deposited on the cathode and oxygen is evolved at the anode. One explanation is that (*a*) aluminium is deposited on the cathode and (*b*) fluorine is released at the anode and then displaces oxygen from Al_2O_3 to give AlF_3. Alternatively, aluminium oxide can be regarded as (at least partly) ionic $(Al^{+++})_2(O^{--})_3$—aluminium ions are deposited on the cathode and oxygen is released at the anode.

(c) **Dilute sulphuric acid** (platinum electrodes)

Result. Hydrogen bubbles off from the cathode and oxygen from the anode. There are 2 volumes of hydrogen for every one of oxygen and the concentration of the acid increases slowly.

$$\begin{array}{ccccc} & & H_2SO_4 & & \\ & & \downarrow & & \\ \text{Cathode} & \longleftarrow & \left\{\begin{array}{c} 2H^+ + SO_4^{--} \\ H^+ + OH^- \end{array}\right\} & \longrightarrow & \text{Anode} \\ 4H^+ + 4e \rightarrow 4[H] & & \upharpoonleft\downharpoonright & & OH^- \text{ selectively} \\ 4[H] \rightarrow 2H_2 & & H_2O & & \text{discharged} \\ & & & & 4OH^- - 4e \rightarrow 4[OH] \\ & & & & 4[OH] \rightarrow 2H_2O + O_2 \end{array}$$

No sulphate ions are discharged and the amount of sulphuric acid remains constant. Because water is removed by electrolysis, the concentration of the acid increases. Consider the quantity of electricity needed to liberate equal volumes of hydrogen and oxygen. One volume of hydrogen is liberated by 2 electrons while 1 volume of oxygen is liberated by 4 electrons, i.e. it requires twice as many electrons to liberate one volume of oxygen as to liberate 1 volume of hydrogen. When a constant current is passed, therefore, the volume of hydrogen to oxygen is 2:1.

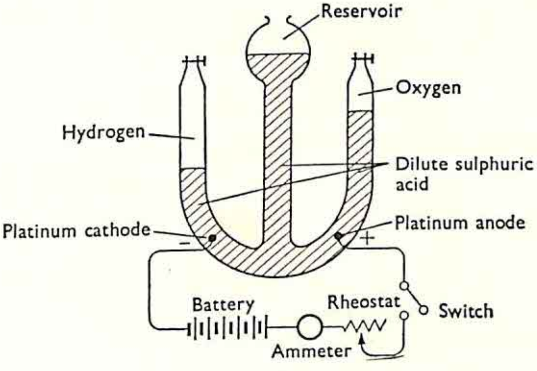


FIG. 3.6

The electrolysis is conveniently carried out in a Hofmann's voltameter (fig. 3.6).

(d) **Cupric sulphate solution** (platinum electrodes)

Result. Copper deposited on the cathode and oxygen bubbles off at the anode. The electrolyte slowly loses its blue colour and is converted to sulphuric acid.

$$\begin{array}{ccccc} & & CuSO_4 & & \\ & & \downarrow & & \\ \text{Cathode} & \longleftarrow & \left\{\begin{matrix} Cu^{++} + SO_4^{--} \\ H^+ + OH^- \end{matrix}\right\} & \longrightarrow & \text{Anode} \\ Cu^{++}\text{ discharged} & & \rightleftharpoons & & OH^-\text{ discharged} \\ 2Cu^{++} + 4e \rightarrow 2Cu & & H_2O & & 4OH^- - 4e \rightarrow 4[OH] \\ & & & & 4[OH] \rightarrow 2H_2O + O_2 \end{array}$$

Since Cu^{++} ions are discharged, but not SO_4^{--} ions, the electrolyte loses its blue colour (due to cupric ions linked to water molecules) and sulphuric acid is formed.

(e) **Cupric sulphate solution** (copper electrodes)

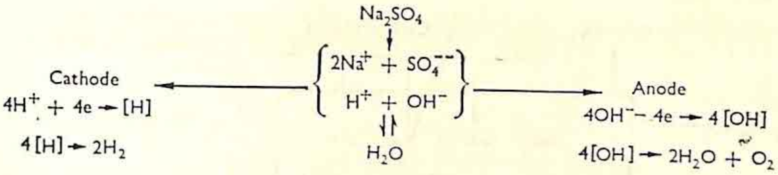
Result. Copper deposited on the cathode and copper dissolved from the anode.

$$\begin{array}{ccccc} & & CuSO_4 & & \\ & & \downarrow & & \\ \text{Cathode} & \longleftarrow & \left\{\begin{matrix} Cu^{++} + SO_4^{--} \\ H^+ + OH^- \\ \rightleftharpoons \end{matrix}\right\} & \longrightarrow & \text{Anode} \\ Cu^{++} + 2e \rightarrow Cu & & H_2O & & \text{The easiest process is} \\ \text{Copper deposited} & & & & Cu \rightarrow Cu^{++} + 2e \\ & & & & \text{(see 3.3), i.e. neither} \\ & & & & OH^-\text{ nor }SO_4^{--}\text{ are} \\ & & & & \text{discharged.} \\ & & & & \text{Copper dissolved} \end{array}$$

The number of Cu^{++} ions formed at the anode is equal to the number discharged at the cathode and the concentration of the electrolyte therefore remains constant. The process has several industrial uses, e.g. the refining of impure copper (the impure metal is made the anode while pure copper constitutes the cathode), and copper plating (the article to be plated is made the cathode and the anode is a copper block).

(f) **Sodium sulphate solution** (platinum electrodes)

Result. Hydrogen bubbles off at the cathode and oxygen at the anode. Sulphuric acid forms near the anode and sodium hydroxide near the cathode.



In the region of the anode, sulphate ions are present. The removal of hydroxide ions upsets the equilibrium of the water molecules with hydrogen and hydroxide ions and this causes more water molecules to ionize, an excess of hydrogen ions building up near the anode (see 3.1). Hence, sulphuric acid is present near the anode.

In a similar manner, sodium ions are present near the cathode. The discharge of hydrogen ions causes the hydroxide ion concentration to increase, showing that sodium hydroxide is present.

The electrolysis can be carried out in the apparatus shown in fig. 3.7.

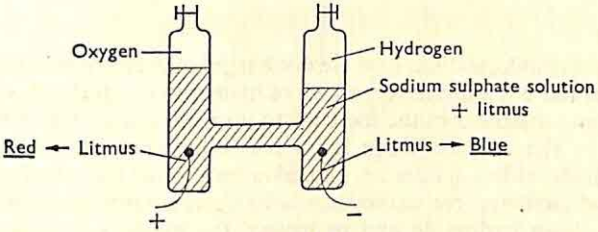


FIG. 3.7

(g) Sodium chloride solution (brine)

1. If dilute brine is electroylsed with platinum electrodes, hydrogen is liberated at the cathode and oxygen at the anode as in example (*f*).
2. If concentrated brine is electrolysed under the correct conditions, the following chemicals can be obtained: sodium hydroxide, chlorine, hydrogen, sodium hypochlorite, sodium chlorate.

One way in which the first three of these chemicals can be made is by the Castner-Kellner cell (flowing mercury cathode cell).

The anode is of carbon and the cathode is a stream of mercury flowing along the slightly sloping floor.

At the anode, chloride ions are discharged in preference to hydroxyl ions since the former are in much higher concentration.

$$Cl^- \rightarrow Cl + e, \qquad 2Cl \rightarrow Cl_2$$

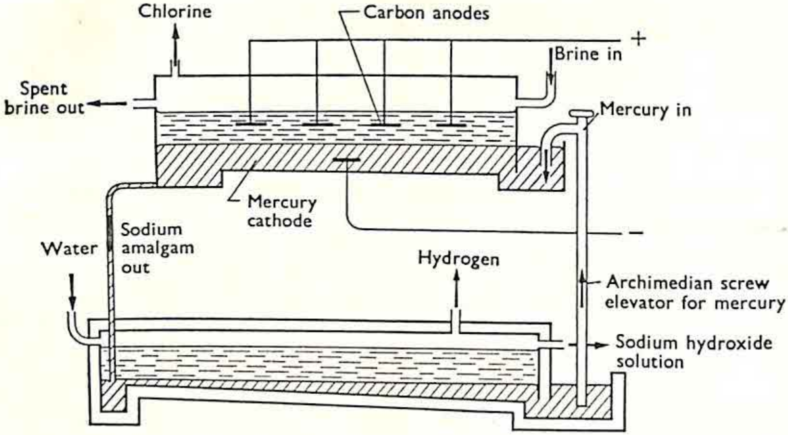


FIG. 3.8

At the cathode, sodium ions are discharged in preference to hydrogen ions since there is a high overvoltage of hydrogen at a mercury cathode. The sodium dissolves in the mercury to give sodium amalgam which is led out of the cell, i.e. there is no possibility that the chlorine and sodium hydroxide will interact, and taken to another cell which contains water and auxiliary iron cathodes. Under these conditions the amalgam forms sodium hydroxide and hydrogen, the mercury liberated being recirculated to the main cell.

$$\underset{\substack{\text{sodium amalgam}\\\text{(representation only)}}}{2Na/Hg} + 2H_2O \rightarrow 2NaOH + H_2\uparrow$$

3. If concentrated brine is electrolysed at 0°C and the contents of the cell are stirred, sodium hypochlorite and sodium chloride are formed. They can be separated by fractional crystallization.

$$2OH^- + Cl_2 \rightarrow \underset{\substack{\text{hypochlorite}\\\text{ion}}}{OCl^-} + \underset{\substack{\text{chloride}\\\text{ion}}}{Cl^-} + H_2O \qquad (1)$$

$$(\text{or } 2NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O)$$

If concentrated brine at 70°C is electrolysed and the contents of the cell are stirred, sodium chlorate and sodium chloride are formed. They can be separated by fractional crystallization.

The reaction is essentially an oxidation-reduction between hypochlorite ions initially formed.

$$\mathrm{OCl^- + 2OCl^- \rightarrow \underset{\substack{\text{chlorate}\\\text{ion}}}{ClO_3^-} + \underset{\substack{\text{chloride}\\\text{ion}}}{2Cl^-}} \qquad (2)$$

$$\text{(or } \mathrm{NaOCl + 2NaOCl \rightarrow NaClO_3 \quad 2NaCl}\text{)}$$

If equation (2) is added to three times (1), the sodium hypochlorite is eliminated giving

$$\mathrm{6OH^- + 3Cl_2 \rightarrow ClO_3^- + 5Cl^- + 3H_2O}$$
$$\text{(or } \mathrm{6NaOH + 3Cl_2 \rightarrow NaClO_3 + 5NaCl + 3H_2O}\text{)}$$

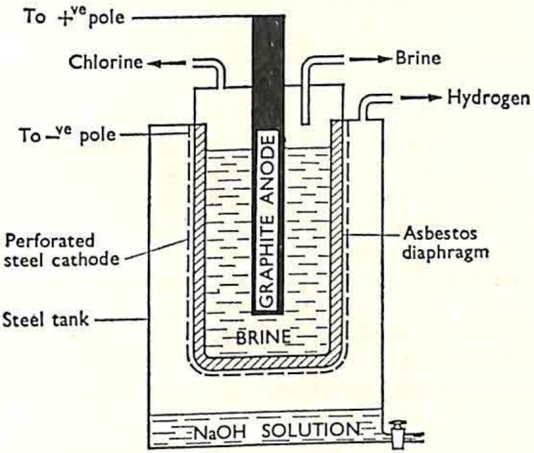


FIG. 3.9

Another type of cell is the *diaphragm cell* (fig. 3.9). The solution in the anode compartment contains Na^+ and Cl^- ions, together with H^+ and OH^- ions from water. On electrolysis:

$$\oplus \longleftarrow \left\{\begin{matrix}\mathrm{Cl^-Na^+}\\ \mathrm{OH^-H^+}\end{matrix}\right\} \longrightarrow \ominus$$

Cl^- discharged
(in higher concⁿ)
↓
Cl_2
(collected)

H^+ discharged → H_2 (collected) Na^+ ion concⁿ increases in region of cathode, liberation of H^+ ions causes an increase in the concⁿ of OH^- ions

The accumulation of Na^+ and OH^- ions round the cathode means that the solution which trickles through the diaphragm and cathode is, in effect, sodium hydroxide solution.

3.5 QUESTIONS

1. Work out the products of electrolysis of separate solutions of silver nitrate ($Ag^+NO_3^-$) and concentrated hydrochloric acid (H^+Cl^-).
2. What volume of hydrogen would be evolved at N.T.P. by the electrolysis of dilute sulphuric acid (platinum electrodes), if the current is 2 amps for 1 hour? [835 cm³]
3. What weight of chlorine is produced per hour in a Castner-Kellner cell which uses a current of 10,000 amps? [13·245 kg]
4. What total volume of 'electrolytic gas' would be liberated at N.T.P. from dilute sulphuric acid by a current which, flowing for the same time, deposits 0·315 g of copper from cupric sulphate solution? [168 cm³]
5. An electric current is passed through two voltameters in series containing respectively, cupric sulphate solution and water acidified with sulphuric acid. After the current had passed for a certain time, 0·124 g of copper had been deposited on the cathode and 47·0 cm³ of hydrogen, measured at 15°C and 740 mm, had been liberated. Deduce the gram equivalent weight of copper. [31·8]
6. An electric current is passed through two voltameters in series. One has silver electrodes and contains silver nitrate solution whilst the other has platinum electrodes and contains dilute sulphuric acid. If 4·32 g of silver are found to be deposited in the first, what volume of hydrogen (at 72 cm and 27°C) is produced in the second? [522 cm³]

4 Redox

4.1 MEANING OF OXIDATION AND REDUCTION

Oxidation is defined as the addition of oxygen atoms to an element or compound, removal of hydrogen atoms from a compound, increasing the electronegative part of a compound (or decreasing the electropositive part), or removal of electrons from an atom or ion. A substance capable of causing another substance to be oxidized is called an *oxidizing agent.*

Reduction is the opposite. It is defined as the removal of oxygen atoms from, or addition of hydrogen atoms to, a substance, increasing the electropositive part of a compound (or decreasing the electronegative part), or addition of electrons to an atom or ion. A substance capable of causing another substance to be reduced is called a *reducing agent.*

The definitions of oxidation or reduction often overlap, e.g. it is possible that addition of oxygen to a substance also involves the removal of electrons from an atom or ion.

4.2 EXAMPLES OF OXIDATION AND REDUCTION

(*a*) When an atom of a metal loses electrons, the process is an oxidation because electrons are *given up* in the formation of a cation, for example:

$$\mathrm{Na} \rightarrow \mathrm{Na}^+ + \mathrm{e} \quad (\mathrm{e} = \text{electron})$$

(*b*) If electrons are added to a positive ion to give a neutral atom, the process is a reduction since electrons are *added*, for example:

$$\mathrm{Na}^+ + \mathrm{e} \rightarrow \mathrm{Na}$$

This type of change occurs at the cathode in electrolysis.

(*c*) If electrons are added to an atom in the formation of an anion, the process is a reduction since electrons are *added*, for example:

$$\mathrm{Cl} + \mathrm{e} \rightarrow \mathrm{Cl}^-$$

(*d*) If electrons are removed from a negative ion forming a neutral atom, the process is an oxidation since electrons are *removed*, for example:

$$\mathrm{Cl}^- - \mathrm{e} \rightarrow \mathrm{Cl}$$

This type of process occurs at the anode during electrolysis.

(*e*) Consider the reaction between ferric chloride and stannous chloride to give ferrous chloride and stannic chloride.

$$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$$
$$2Fe^{+++} + Sn^{++} \rightarrow 2Fe^{++} + Sn^{++++}$$

Each stannous ion has lost two electrons and has therefore been oxidized. Each ferric ion has gained one electron and has therefore been reduced.

In every reaction of this sort which involves an oxidation, there must be a corresponding reduction. *Oxidation and reduction are complementary and the one process cannot take place without the other.* The system as a whole is referred to as a *Redox Reaction.*

(*f*) Consider the reaction between potassium iodide solution and chlorine to give potassium chloride solution and iodine.

$$2KI + Cl_2 \rightarrow 2KCl + I_2$$
$$2I^- + Cl_2 \rightarrow 2Cl^- + I_2$$

Each iodide ion has lost an electron and has therefore been oxidized (the iodine atoms formed unite to give iodine molecules). Each chlorine atom (from a chlorine molecule) has gained an electron and has therefore been reduced.

(*g*) In the reaction between hot cupric oxide and hydrogen to give copper and water, the cupric oxide is reduced to copper since it has lost an oxygen atom, while the hydrogen has been oxidized since it has gained an oxygen atom. The reaction amounts to a competition between a copper atom and a hydrogen molecule for an oxygen atom.

$$CuO + H_2 \rightarrow Cu + H_2O$$

(*h*) In the reaction between hydrogen peroxide and acidified potassium iodide, iodide ions are oxidized to iodine while hydrogen peroxide is reduced to water.

$$2KI + H_2O_2 + 2HCl \rightarrow 2KCl + 2H_2O + I_2$$
$$2I^- + H_2O_2 + 2H^+ \rightarrow 2H_2O + I_2$$

(*i*) In the reaction between potassium permanganate and ferrous sulphate in acid solution, permanganate ions are reduced to manganous ions (electrons are added to what is effectively a manganese atom having a valency of 7 to give a manganese atom with a valency of 2) while ferrous ions are oxidized to ferric ions.

$$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5Fe_2(SO_4)_3$$
$$MnO_4^- + 8H^+ + 5Fe^{++} \rightarrow Mn^{++} + 4H_2O + 5Fe^{+++}$$

← total of 17 electrons involved → ← total of 17 electrons involved →

(*j*) In the reaction between zinc and dilute sulphuric acid, zinc is oxidized to zinc ions while hydrogen ions (from the acid) are reduced to hydrogen atoms (which then unite to give molecules).

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2\uparrow$$
$$Zn + 2H^+ \rightarrow Zn^{++} + H_2\uparrow$$

4.3 OXIDIZING AND REDUCING EQUATIONS

It is possible to build up redox equations from simpler equations which show the way or ways in which a substance can act as an oxidizing or reducing agent. In some cases, oxidizing equations are written in terms of oxygen or hydrogen provided for oxidation or reduction, written [O] and [H]. In other cases it is more convenient to write the equations in terms of *electron transfer*. In most cases, the equations can be written in both ways.

Examples (oxidizing equations)

1. Oxygen, $O_2 \rightarrow 2[O]$
2. Ozone, $O_3 \rightarrow O_2 + [O]$
3. Hydrogen peroxide, $H_2O_2 \rightarrow H_2O + [O]$
4. Hot concentrated sulphuric acid, $H_2SO_4 \rightarrow H_2O + SO_2 + [O]$
5. Concentrated nitric acid, $2HNO_3 \rightarrow H_2O + 2NO_2 + [O]$
6. Manganese dioxide, $MnO_2 \rightarrow MnO + [O]$
7. Chlorine water, $Cl_2 + H_2O \rightarrow HCl + \underset{\displaystyle HCl + [O]}{\underset{\downarrow}{HOCl}}$
8. Potassium permanganate in acid solution,
   $2KMnO_4 + 4H_2SO_4 \rightarrow 2KHSO_4 + 2MnSO_4 + 3H_2O + 5[O]$
9. Potassium dichromate in acid solution,
   $K_2Cr_2O_7 + 5H_2SO_4 \rightarrow 2KHSO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$

Many of the above equations can be expressed conveniently in terms of electron transfer.

3. Assuming that acid is present, $H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O$
4. $H_2SO_4 + 2H^+ + 2e \rightarrow 2H_2O + SO_2$
5. $2HNO_3 + 2H^+ + 2e \rightarrow 2H_2O + 2NO_2$
6. Assuming that acid is present,
   $MnO_2 + 4H^+ + 2e \rightarrow Mn^{++} + 2H_2O$
8. $MnO_4^- + 8H^+ + 5e \rightarrow Mn^{++} + 4H_2O$
9. $Cr_2O_7^{--} + 14H^+ + 6e \rightarrow 2Cr^{+++} + 7H_2O$

It should be noticed that chlorine acts as an oxidizing agent by taking hydrogen atoms from substances.

$$Cl_2 + 2[H] \rightarrow 2HCl$$

Sulphur dioxide, although normally a reducing agent, can also act as an oxidizing agent.

$$SO_2 \rightarrow S + 2[O]$$

Examples (reducing equations)

1. Hydrogen, $H_2 + [O] \rightarrow H_2O$
2. Carbon monoxide, $CO + [O] \rightarrow CO_2$
3. Carbon, $C + [O] \rightarrow CO$
4. Hydrogen sulphide, $H_2S + [O] \rightarrow H_2O + S$
5. Sulphur dioxide, $SO_2 + [O] + H_2O \rightarrow H_2SO_4$
6. Hydrogen iodide, $2HI + [O] \rightarrow H_2O + I_2$
7. Acidified ferrous sulphate,
$$2FeSO_4 + H_2SO_4 + [O] \rightarrow Fe_2(SO_4)_3 + H_2O$$
8. Oxalic acid, $(COOH)_2 + [O] \rightarrow 2CO_2 + H_2O$

Some of the above reactions can be represented conveniently in terms of electron transfer.

5. $2H_2O + SO_2 - 2e \rightarrow H_2SO_4 + 2H^+$
7. $Fe^{++} - e \rightarrow Fe^{+++}$

Notice that some reducing equations can be written in terms of the donation of hydrogen atoms, instead of the removal of oxygen atoms, e.g.

1. Hydrogen, $H_2 \rightarrow 2[H]$
4. Hydrogen sulphide, $H_2S \rightarrow 2[H] + S$
5. Hydrogen iodide, $2HI \rightarrow 2[H] + I_2$

4.4 CONSTRUCTION OF REDOX EQUATIONS

Oxygen for oxidation, hydrogen for reduction, or electrons must not appear in the final equation.

Examples

1. Manganese dioxide with hot concentrated hydrochloric acid

$$\begin{array}{ll} & MnO_2 \rightarrow MnO + [O] \\ & 2HCl + [O] \rightarrow H_2O + Cl_2 \\ \text{also} & MnO + 2HCl \rightarrow MnCl_2 + H_2O \\ \hline & MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2 \\ \hline \end{array}$$

Alternatively

$$\begin{array}{l} MnO_2 + 4H^+ + 2e \rightarrow Mn^{++} + 2H_2O \\ 2Cl^- - 2e \rightarrow Cl_2 \\ \hline MnO_2 + 4H^+ + 2Cl^- \rightarrow Mn^{++} + 2H_2O + Cl_2 \\ \hline \end{array}$$

2. Copper and concentrated nitric acid

$$\begin{array}{l} 2HNO_3 \rightarrow H_2O + 2NO_2 + [O] \\ Cu + [O] \rightarrow CuO \\ CuO + 2HNO_3 \rightarrow Cu(NO_3)_2 + H_2O \\ \hline Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2 \\ \hline \end{array}$$

Alternatively

$$\begin{array}{l} 2HNO_3 + 2H^+ + 2e \rightarrow 2NO_2 + 2H_2O \\ Cu - 2e \rightarrow Cu^{++} \\ \hline Cu + 2HNO_3 + 2H^+ \rightarrow 2NO_2 + 2H_2O + Cu^{++} \\ \hline \end{array}$$

$$(\text{or } Cu + 4H^+ + 2NO_3^- \rightarrow 2NO_2 + 2H_2O + Cu^{++})$$

3. The reaction between acidified potassium iodide and hydrogen peroxide

$$\begin{array}{l} H_2O_2 \rightarrow H_2O + [O] \\ 2HI + [O] \rightarrow H_2O + I_2 \quad (\text{N.B. } 2KI + H_2SO_4 \rightarrow K_2SO_4 + 2HI) \\ \hline 2HI + H_2O_2 \rightarrow 2H_2O + I_2 \\ \hline \end{array}$$

Alternatively

$$\begin{array}{l} H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O \\ 2I^- - 2e \rightarrow I_2 \\ \hline H_2O_2 + 2H^+ + 2I^- \rightarrow 2H_2O + I_2 \\ \hline \end{array}$$

4. The reaction between ferric ions and stannous ions in aqueous solution

$$\begin{array}{l} 2Fe^{+++} + 2e \rightarrow 2Fe^{++} \\ Sn^{++} - 2e \rightarrow Sn^{++++} \\ \hline 2Fe^{+++} + Sn^{++} \rightarrow 2Fe^{++} + Sn^{++++} \\ \hline \end{array}$$

5. The reaction between zinc and cupric ions in aqueous solution

$$\begin{array}{l} Zn - 2e \rightarrow Zn^{++} \\ Cu^{++} + 2e \rightarrow Cu \\ \hline Zn + Cu^{++} \rightarrow Zn^{++} + Cu \\ \hline \end{array}$$

6. The reaction between acidified potassium permanganate and ferrous sulphate

$$\begin{array}{l} MnO_4^- + 8H^+ + 5e \rightarrow Mn^{++} + 4H_2O \\ 5Fe^{++} - 5e \rightarrow 5Fe^{+++} \\ \hline MnO_4^- + 8H^+ + 5Fe^{++} \rightarrow Mn^{++} + 4H_2O + 5Fe^{+++} \\ \hline \end{array}$$

4.5 OXIDATION STATE

The oxidation state of an element in a compound is defined as the number of electrons lost or gained relative to the elemental state. Thus in chlorine Cl_2, the chlorine atom is in the zero oxidation state, in chloride ion Cl^- it is in the -1 state since the atom has gained one electron, while in hypochlorous acid H^+OCl^- the chlorine must be in the $+1$ oxidation state in order that the net charge on the hypochlorite ion is a single negative (consider this ion as $O^{--}Cl^+$). The importance of knowing the oxidation state is evident when we consider two compounds such as potassium ferrocyanide $K_4Fe(CN)_6$ and potassium ferricyanide $K_3Fe(CN)_6$. Both compounds give an anion in which the iron atom is surrounded by six cyanide ions, but the oxidation states of the iron are $+2$ and $+3$ respectively. We can write them $(K^+)_4[Fe^{II}(CN)_6]$ and $(K^+)_3[Fe^{III}(CN)_6]$.

4.6 QUESTIONS

1. Describe any five typical redox reactions, pointing out which is the oxidizing agent and which is the reducing agent in each case.
2. Describe one reaction of each of the following substances showing how it can behave as a reducing agent: ammonia, hydrogen, hydrogen sulphide, hydrogen chloride, sulphur dioxide.

5 The Electrochemical Series

You will no doubt realize that the elements differ in how 'grasping' they are, i.e. the way in which they compete for one another. Thus, the metals iron, magnesium, lead, zinc, sodium, calcium, mercury, and copper might be heated in air and then arranged in order of their affinity for oxygen as judged by the vigour with which they burn or are oxidized in the air. Also, a 'vigorous' metal can rob a less vigorous one of its oxygen (e.g. if copper oxide is heated with magnesium powder, magnesium oxide is formed and when ferric oxide is heated with aluminium powder, iron is formed—thermite process). It is also possible to place carbon in the list of order of affinity for oxygen. A similar picture is true for the reactions between metals and sulphur.

This difference of reactivity of the metals, not only with oxygen, but also with water, acids, etc, is the subject of this chapter.

5.1 THE SERIES

The elements are arranged in decreasing order of their chemical reactivity, the series being of greatest value for metallic elements.

It is really a redox series which places the metals in decreasing order of their reducing power, i.e. the ones near the top are readily oxidized to their ions while those at the bottom are not so readily oxidized. In a more advanced textbook, you will learn that the metals are listed in decreasing order of their 'electrode potentials' (hence the name electrochemical series). For the moment you can think of an electrode potential as something which measures the tendency of an element to be oxidized or reduced.

Table 5.1

Metal	*Redox process*
Potassium	$K \rightleftharpoons K^+ + e$
Sodium	$Na \rightleftharpoons Na^+ + e$
*Calcium	$Ca \rightleftharpoons Ca^{++} + 2e$
Magnesium	$Mg \rightleftharpoons Mg^{++} + 2e$
Aluminium	$Al \rightleftharpoons Al^{+++} + 3e$
Zinc	$Zn \rightleftharpoons Zn^{++} + 2e$

* According to the redox potential, calcium lies above sodium, but from the point of view of reactivity it is better to reverse the order.

Metal	*Redox process*
Iron	$Fe \rightleftharpoons Fe^{++} + 2e$
Tin	$Sn \rightleftharpoons Sn^{++} + 2e$
Lead	$Pb \rightleftharpoons Pb^{++} + 2e$
*Hydrogen	$H \rightleftharpoons H^{+} + e$
Copper	$Cu \rightleftharpoons Cu^{++} + 2e$
Mercury	$Hg \rightleftharpoons Hg^{++} + 2e$
Silver	$Ag \rightleftharpoons Ag^{+} + e$

* Hydrogen is not a metal, but provides a convenient boundary in the series.

The electropositivity (2.11) decreases in passing down the series. The series helps to bring order to the properties of the metals.

5.2 OCCURRENCE OF METALS

In general, the most electropositive metals combine with the most electronegative elements in minerals. Thus, sodium is combined with chlorine in sodium chloride, aluminium is combined with oxygen in aluminium oxide, while zinc, lead, copper, mercury and silver are combined with sulphur in sulphide minerals.

5.3 EXTRACTION OF METALS

In order to extract a metal from its mineral, a reduction process is needed since the electronegative part of the mineral must be decreased. The metals from potassium to aluminium are normally extracted by electrolytic reduction of the metal ion, for example

$$Na^{+} + 1e \rightarrow Na$$

Compared with the countries using 'white power' from snow → dam → power station, electricity is a last resort in Great Britain, e.g. the manufacturers of magnesium can barely compete with the continental manufacturers in this field.

Zinc can be obtained by electrolytic reduction of the zinc ion in zinc sulphate solution, although it is also obtained by reduction of the oxide (obtained from the sulphide ore) with hot carbon. The zinc and carbon compete for oxygen and carbon wins, leaving zinc as the metal.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$
$$ZnO + C \rightarrow Zn + CO\uparrow$$

The metals from zinc to lead are obtained by conversion of the mineral in the ore to an oxide followed by reduction with hot carbon or carbon monoxide. Thus, iron is obtained in the blast furnace where the main reaction is

$$Fe_2O_3 + 3CO \rightleftharpoons 2Fe + 3CO_2$$

Mercury is obtained merely by roasting the sulphide ore in air, since mercuric oxide is unstable when heated.

$$2HgS + 3O_2 \rightarrow 2HgO + 2SO_2$$
$$2HgO \rightarrow 2Hg + O_2\uparrow$$

Metals right at the bottom of the series (silver, gold) are so unreactive that they occur as the metal in an uncombined state.

Extraction of metals using electrolytic cells

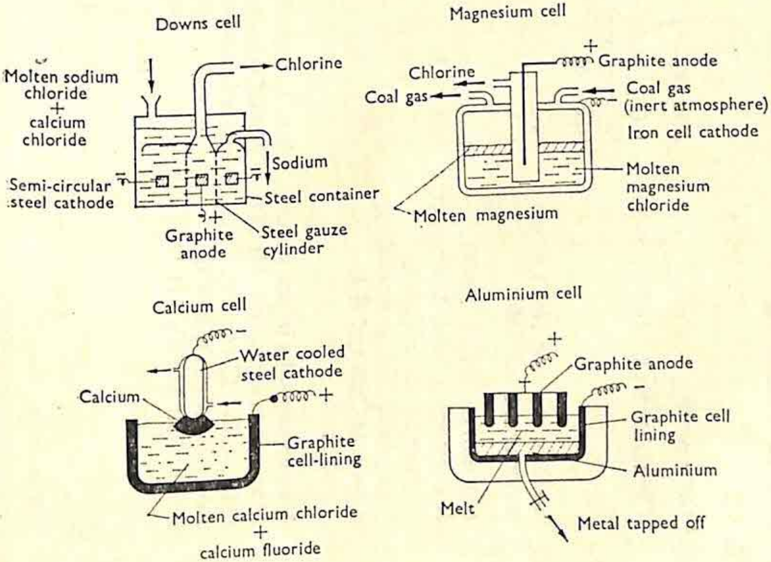


FIG. 5.1

The ease of extraction therefore increases in passing down the series, i.e. in the decreasing order of stability of the metallic ion.

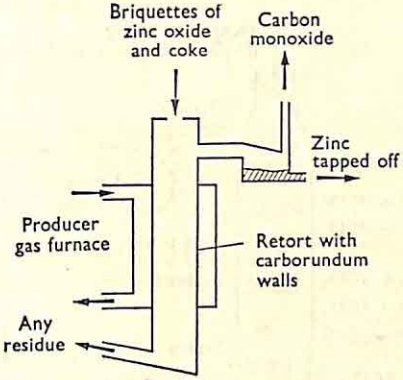
Table 5.2

Metal	*Occurrence*	*Source for extraction*	*Extraction*
K	Carnallite $KCl.MgCl_2.6H_2O$	KCl, obtained from Carnallite by fractional crystallization (see 1.6)	Electrolysis of fused KCl
Na	Sodium chloride NaCl in sea water and Rock salt	NaCl	Electrolysis of fused NaCl (see fig. 5.1)
Ca	Calcium carbonate $CaCO_3$ (Limestone, Chalk, Marble, etc), calcium sulphate $CaSO_4$ (Anhydrite), calcium sulphate dihydrate $CaSO_4.2H_2O$ (Gypsum)	$CaCl_2$ from the Solvay process (see 19.3)	Electrolysis of fused $CaCl_2$ (see fig. 5.1)
Mg	Magnesium salts in sea water, Magnesium carbonate $MgCO_3$ (Magnesite), Carnallite, Dolomite $MgCO_3.CaCO_3$ Epsom Salt $MgSO_4$ $7H_2O$	$MgCl_2$ from Carnallite, or $Mg(OH)_2$ obtained when calcium oxide is added to sea water $Mg^{++} + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + Ca^{++}$ $(Ca^{++} + 2OH^-)$ $\uparrow H_2O$ CaO	(*a*) Electrolysis of fused $MgCl_2$ (fig. 5.1); this is obtained from $Mg(OH)_2$ by first heating it to give the oxide and then heating this with carbon and chlorine $MgO + C + Cl_2 \rightarrow MgCl_2 + CO$ (*b*) Reduction of molten $MgCl_2$ by sodium (*c*) Reduction of Dolomite by heating with the alloy 'ferrosilicon'

Al	Alumina Al_2O_3 (Bauxite), sodium fluoaluminate $(Na^+)_3AlF_6^{3-}$ (Cryolite)	Pure alumina; Bauxite is freed from ferric oxide by dissolving the alumina in sodium hydroxide solution; some pure aluminium hydroxide is added to the filtrate which precipitates all the aluminium as its hydroxide leaving sodium silicate (from silica in the Bauxite) unaffected; the hydroxide is heated to give the oxide	Electrolysis of Al_2O_3 in molten Cryolite (see fig. 5.1)
Zn	Zinc sulphide ZnS (Zinc Blende), Zinc carbonate $ZnCO_3$ (Calamine)	ZnO from ZnS or $ZnCO_3$	Reduction of ZnO by hot carbon in a vertical retort or blast furnace. Also by electrolysis of $ZnSO_4$ solution using a lead anode and aluminium cathode; hydrogen is not discharged at the cathode since it has a high overvoltage on zinc
Fe	Ferric oxide Fe_2O_3 (Haematite), Ferroso-ferric oxide Fe_3O_4 (Magnetite), Iron pyrites FeS_2	Fe_2O_3, Fe_3O_4	Reduction of oxide by carbon monoxide in the blast furnace. Limestone is added to give a slag with silica impurities. $CaCO_3 \rightarrow CaO + CO_2$ $CaO + SiO_2 \rightarrow CaSiO_3$ Brittle cast (pig) iron is obtained

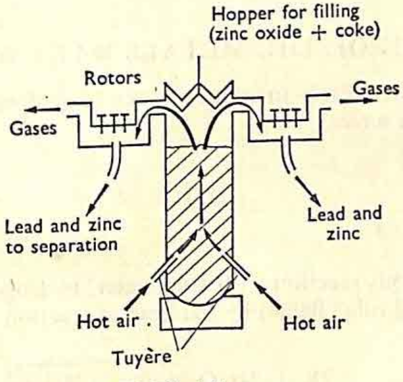
Metal	*Occurrence*	*Source for extraction*	*Extraction*
Sn	Stannic oxide SnO_2 (Cassiterite, Tinstone)	SnO_2	Reduction of SnO_2 with hot carbon
Pb	Lead sulphide PbS (Galena)	PbO obtained by roasting PbS in air	Reduction of PbO with hot carbon
Cu	Copper pyrites $CuFeS_2$	Cu_2S (from $CuFeS_2$)	Reduction of Cu_2O (from Cu_2S) with more Cu_2S. The metal is purified by electrolysis (3.4)
Hg	Mercuric sulphide HgS (Cinnabar)	HgS	Reduction of HgS by heating it in air
Ag	Silver metal, Silver sulphide Ag_2S (Argentite)	Ag, Ag_2S	Complex procedure of extraction from Ag_2S; the ore is digested in sodium cyanide solution to give sodium argentocyanide $Na^+Ag(CN)_2^-$ and silver is precipitated by addition of zinc in alkaline solution

Extraction of zinc


Briquettes of zinc oxide and coke
Carbon monoxide
Zinc tapped off
Producer gas furnace
Retort with carborundum walls
Any residue

(a) Vertical retort

N.B.: The briquettes have just (additional cost) to be prepared for use in the vertical retort; the charge must be sufficiently strong mechanically to avoid choking of the base with 'fines'.


Hopper for filling (zinc oxide + coke)
Rotors
Gases
Gases
Lead and zinc to separation
Lead and zinc
Hot air
Hot air
Tuyère

(b) Blast furnace

Zinc is volatile at the temperature of the furnace and leaves with the furnace gases. Since the concentration of zinc in the gases is so low, it is condensed out with molten lead, sprayed up with rotors. On cooling, the molten mixture of zinc and lead releases zinc which floats on the surface. The process can be worked for lead as well as zinc (ZnS and PbS often cccur together)

FIG. 5.2

The iron blast furnace

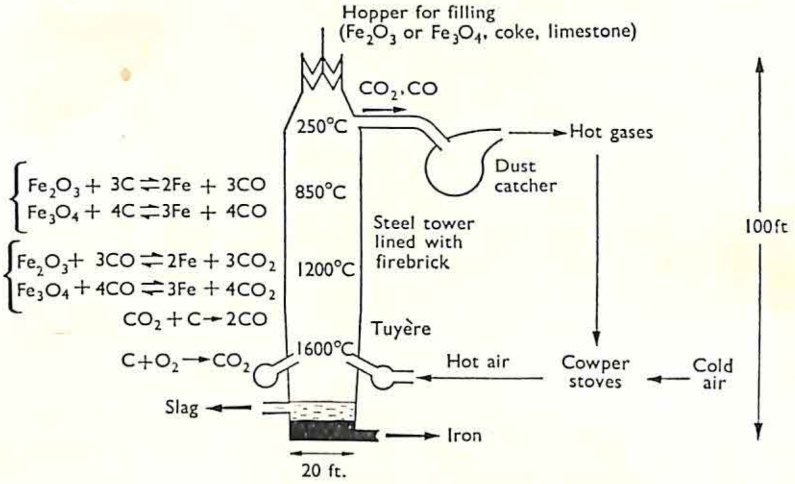

Hopper for filling
(Fe_2O_3 or Fe_3O_4, coke, limestone)
CO_2, CO
250°C
Hot gases
Dust catcher
$Fe_2O_3 + 3C \rightleftharpoons 2Fe + 3CO$
$Fe_3O_4 + 4C \rightleftharpoons 3Fe + 4CO$
850°C
Steel tower lined with firebrick
100ft
$Fe_2O_3 + 3CO \rightleftharpoons 2Fe + 3CO_2$
$Fe_3O_4 + 4CO \rightleftharpoons 3Fe + 4CO_2$
1200°C
$CO_2 + C \rightarrow 2CO$
Tuyère
1600°C
$C + O_2 \rightarrow CO_2$
Hot air
Cowper stoves
Cold air
Slag
Iron
20 ft.

FIG. 5.3

5.4 REACTION OF THE METALS WITH WATER

The ability of the metals to reduce water to hydrogen decreases in passing down the series.

Table 5.3

Metal	*Reaction*
K	Vigorous reaction with cold water, hydrogen evolved being ignited (lilac flame) by the heat of reaction $2K + 2H_2O \rightarrow \underset{\text{potassium hydroxide}}{\overbrace{2K^+ + 2OH^-}} + H_2\uparrow$
Na	Vigorous reaction with cold water; if the motion of the metal on the surface of the water is restricted, the hydrogen ignites (yellow flame) $2Na + 2H_2O \rightarrow \underset{\text{sodium hydroxide}}{\overbrace{2Na^+ + 2OH^-}} + H_2\uparrow$

Ca Fairly vigorous reaction with cold water but the hydrogen does not ignite

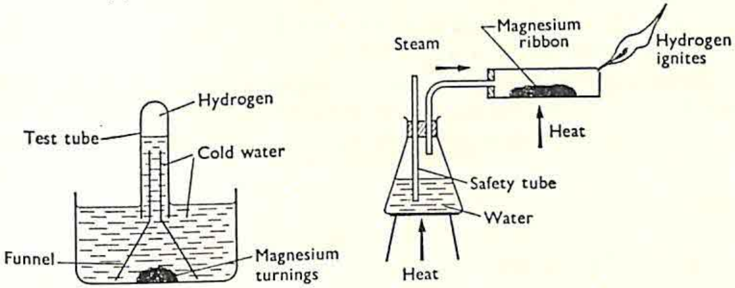
$$\mathrm{Ca} + 2\mathrm{H_2O} \rightarrow \underset{\text{calcium hydroxide}}{\overbrace{\mathrm{Ca^{++}} + 2\mathrm{OH^{-}}}} + \mathrm{H_2}\uparrow$$

Mg (*a*) Reacts very slowly with cold water to give hydrogen

$$\mathrm{Mg} + \mathrm{H_2O} \rightarrow \underset{\text{magnesium oxide}}{\mathrm{MgO}} + \mathrm{H_2}\uparrow$$

(*b*) Reacts more vigorously with warm water

(*c*) It burns in steam



(a) Reaction of Mg with cold water (b) Burning of Mg in steam

FIG. 5.4

Al
Zn
Fe No reaction with cold water (although iron rusts in the presence of air) or warm water, but the hot metals react with steam to some extent

Action of steam on red-hot iron

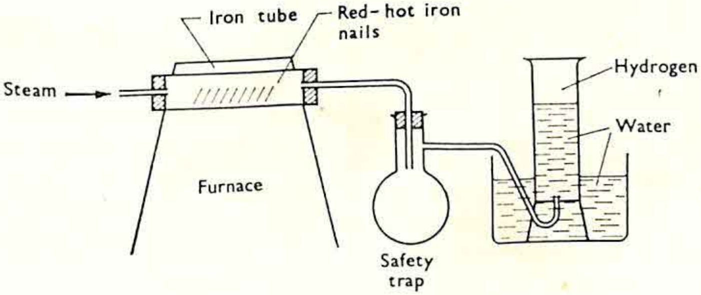


FIG. 5.5

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$$
$$Zn + H_2O \rightarrow ZnO + H_2$$
$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$

Sn Pb Cu Hg Ag	No reaction with water, even when the metal is hot and steam is used. Lead, however, is attacked by water containing carbonic acid (e.g. soft moorland water) but it is not attacked by hard water or water in the absence of air

5.5 DISPLACEMENT OF METALS FROM SOLUTION

A metal high in the series will displace any lower metal from a solution of any salt of the lower metal.

These displacements are really reduction reactions of metal ions to metal atoms. Thus, zinc is a better reducing agent than copper and will therefore reduce cupric ions (in, say, cupric sulphate solution) to copper.

$$Zn + Cu^{++} \rightarrow Zn^{++} + Cu\downarrow$$

5.6 REACTION OF THE METALS WITH DILUTE MINERAL ACIDS

All metals above hydrogen in the series reduce hydrogen ions in dilute hydrochloric or sulphuric acid to give hydrogen, the ease decreasing in passing from potassium (violent reaction) to lead (hardly any reaction; this is due partly to the fact that lead chloride and sulphate are only sparingly soluble in water and therefore coat on the surface of metal, preventing much reaction), for example:

$$Mg + 2H^+ \rightarrow Mg^{++} + H_2\uparrow$$
$$2Al + 6H^+ \rightarrow 2Al^{+++} + 3H_2\uparrow$$

Kipp's apparatus

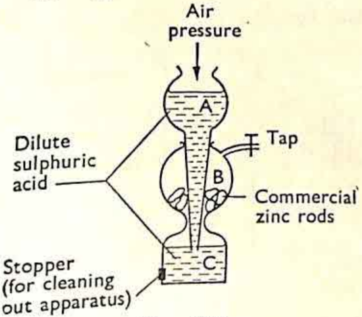


FIG. 5.6

Zinc and dilute sulphuric acid are normally used in the laboratory preparation of hydrogen since the metal is fairly cheap and hydrogen is produced at a reasonable rate. The reaction is done in a Kipp's apparatus.

$$Zn + 2H^+ \rightarrow Zn^{++} + H_2\uparrow$$

(When the tap is turned on the air pressure forces acid into chamber B from chamber A via chamber C. When the tap is turned off, the pressure of gas in B forces acid back into A again.)

Metals below hydrogen in the series have no reaction with dilute hydrochloric or sulphuric acids.

Dilute nitric acid reacts with all the metals given in the series (but not with gold) to give nitrates, but no hydrogen is formed; nitric acid is a much more vigorous oxidizing agent than the other two acids mentioned, for example:

$$\begin{array}{l} \overbrace{10H^+ + 10NO_3^-} + 8e \rightarrow 3H_2O + \overbrace{NH_4^+ + NO_3^-} + 8NO_3^- \\ 4Zn \rightarrow 4Zn^{++} + 8e \\ \hline 4Zn + \overbrace{10H^+ + 10NO_3^-} \rightarrow \overbrace{4Zn^{++} + 8NO_3^-} + \overbrace{NH_4^+ + NO_3^-} + 3H_2O \\ \hline \end{array}$$

For example:

$$\begin{array}{l} \overbrace{8H^+ + 8NO_3^-} + 6e \rightarrow 2NO + 4H_2O + 6NO_3^- \\ 3Cu \rightarrow 3Cu^{++} + 6e \\ \hline 3Cu + \overbrace{8H^+ + 8NO_3^-} \rightarrow \overbrace{3Cu^{++} + 6NO_3^-} + 4H_2O + 2NO\uparrow \\ \hline \end{array}$$

5.7 REACTION OF THE METALS WITH AIR (OR OXYGEN)

The reaction of a metal with oxygen depends upon the readiness with which the metal is oxidized to its ion. Not all metallic oxides are ionic compounds, however, since some measure of covalency may be present in the bonding owing to the influence of the metal ion on the oxide ion.

In table 5.4, oxides with exceptionally high percentages of ionic bonding have been written with an ionic formula. Others have been written with the older conventional type of formula; either method may be adopted (from their known crystal structures) to write the formulae of many of them, for example

$$(Al^{+++})_2(O^{--})_3, \qquad Pb^{++}O^{--}, \qquad Cu^{++}O^{--}, \qquad (Cu^+)_2O^{--}$$

Table 5.4

Metal	*Reaction*
K	Reacts with air or oxygen at normal temperatures, and burns when heated, forming a superoxide $K + O_2 \rightarrow K^+O_2^-$
Na	Reacts as for potassium, but forms a peroxide $2Na + O_2 \rightarrow (Na^+)_2O_2^{--}$
Ca	Reacts slowly with air or oxygen at normal temperatures, forming the oxide. Burns when heated to give the oxide and (in air) some nitride $2Ca + O_2 \rightarrow 2Ca^{++}O^{--}$ $3Ca + N_2 \rightarrow (Ca^{++})_3(N^{---})_2$
Mg	Burns when heated to give the oxide and (in air) some nitride $2Mg + O_2 \rightarrow 2Mg^{++}O^{--}$ $3Mg + N_2 \rightarrow (Mg^{++})_3(N^{---})_2$
Al	The finely-divided metal burns when heated to give the oxide $4Al + 3O_2 \rightarrow 2Al_2O_3$
Zn	Burns when heated to give the oxide $2Zn + O_2 \rightarrow 2ZnO$
Fe	Forms ferroso-ferric oxide when heated, but without ignition $3Fe + 2O_2 \rightarrow Fe_3O_4$ (or $Fe^{++}(FeO_2^-)_2$)
Sn	Forms stannic oxide when heated, but without ignition $Sn + O_2 \rightarrow SnO_2$
Pb	Forms some lead monoxide (litharge) when heated very strongly $2Pb + O_2 \rightarrow 2PbO$
Cu	Forms some cupric oxide (and a little cuprous oxide) when heated very strongly $2Cu + O_2 \rightarrow 2CuO$ (cupric oxide) $4Cu + O_2 \rightarrow 2Cu_2O$ (cuprous oxide)

Hg Forms the oxide on heating, but reversibly

$$2Hg + O_2 \rightleftharpoons 2HgO \quad \text{(mercuric oxide)}$$

Ag Not attacked by oxygen

5.8 STABILITY OF METALLIC HYDROXIDES

The stability of metallic hydroxides decreases in passing down the series; it is in this order that the stability of the metal ion decreases, for example:

NaOH, KOH melt on heating, but do not decompose

$$Ca(OH)_2 \xrightarrow{\text{about } 540°C} CaO + H_2O$$
$$(\text{or } Ca^{++}(OH^-)_2 \rightarrow Ca^{++}O^{--} + H_2O)$$

$$Cu(OH)_2 \xrightarrow{\text{below } 100°C} CuO + H_2O$$
$$(\text{or } Cu^{++}(OH^-)_2 \rightarrow Cu^{++}O^{--} + H_2O)$$

(Hg and Ag form no hydroxides)

5.9 STABILITY OF SALTS OF OXYACIDS

(carbonates, nitrates, sulphates, etc)

(a) Nitrates

Sodium and potassium nitrates give the nitrite plus oxygen on heating, for example:

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2\uparrow$$
$$(\text{or } 2Na^+NO_3^- \rightarrow 2Na^+NO_2^- + O_2\uparrow)$$

The nitrates of the metals from calcium to copper decompose into the oxide, nitrogen dioxide and oxygen on heating, for example:

$$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2\uparrow + O_2\uparrow$$
$$(\text{or } 2Pb^{++}(NO_3^-)_2 \rightarrow 2Pb^{++}O^{--} + 4NO_2\uparrow + O_2\uparrow)$$

The stability of oxysalts decreases in passing down the series; it is in this order that the stability of the metal ion decreases.

The ease of decomposition increases in passing down the series.

The nitrates of mercury and silver decompose into the metal (since the oxides are not thermally stable), nitrogen dioxide and oxygen on heating, for example:

$$2AgNO_3 \rightarrow 2Ag + 2NO_2\uparrow + O_2\uparrow$$
$$(\text{or } 2Ag^+NO_3^- \rightarrow 2Ag + 2NO_2\uparrow + O_2\uparrow)$$

Nitrates of

K Na	Ca Mg Al Zn Fe Pb Cu give on heating	Hg Ag
Oxygen + a nitrite	Nitrogen dioxide + oxygen + a metallic oxide	Nitrogen dioxide + oxygen + metal

(b) Carbonates

The carbonates of sodium and potassium melt on heating but without decomposition.

The carbonates of the metals from calcium to copper decompose into the oxide and carbon dioxide on heating, the ease increasing in passing down the series, for example:

$$\begin{gathered}
CaCO_3 \rightleftharpoons CaO + CO_2\uparrow \quad \text{(at about 800°C)} \\
(\text{or } Ca^{++}CO_3^{--} \rightleftharpoons Ca^{++}O^{--} + CO_2) \\
PbCO_3 \rightarrow PbO + CO_2\uparrow \quad \text{(at about 350°C)} \\
(\text{or } Pb^{++}CO_3^{--} \rightarrow Pb^{++}O^{--} + CO_2\uparrow) \\
CuCO_3 \rightarrow CuO + CO_2\uparrow \quad \text{(below 100°C)} \\
(\text{or } Cu^{++}CO_3^{--} \rightarrow Cu^{++}O^{--} + CO_2\uparrow)
\end{gathered}$$

The carbonates of mercury and silver are very easily decomposed by heat, giving the metal, carbon dioxide and oxygen (since the oxides are unstable to heat), for example:

$$\begin{gathered}
2Ag_2CO_3 \rightarrow 4Ag + 2CO_2\uparrow + O_2\uparrow \\
(\text{or } 2(Ag^{+})_2CO_3^{--} \rightarrow 4Ag + 2CO_2\uparrow + O_2\uparrow)
\end{gathered}$$

(c) Sulphates

The sulphates of sodium and potassium melt on heating but without decomposition.

The sulphates of the metals from calcium to copper decompose into the oxides and oxides of sulphur on strong heating, the ease increasing in passing down the series, for example:

$$\begin{gathered}
Zn^{++}SO_4^{--} \rightarrow ZnO + SO_3\uparrow \\
\underset{\text{Ferric sulphate}}{(Fe^{+++})_2(SO_4^{--})_3} \rightarrow Fe_2O_3 + SO_3\uparrow \\
\underset{\text{ferrous sulphate}}{2Fe^{++}SO_4^{--}} \rightarrow Fe_2O_3 + SO_2\uparrow + SO_3\uparrow
\end{gathered}$$

N.B. Sodium and potassium bisulphates have unusual initial decomposition products on heating, for example:

$$2\mathrm{K}^+\mathrm{HSO}_4^- \rightarrow \underset{\substack{\text{potassium}\\\text{pyrosulphate}}}{(\mathrm{K}^+)_2\mathrm{S}_2\mathrm{O}_7^{--}} + \mathrm{H}_2\mathrm{O}$$

Then $$(\mathrm{K}^+)_2\mathrm{S}_2\mathrm{O}_7^{--} \rightarrow (\mathrm{K}^+)_2\mathrm{SO}_4^{--} + \mathrm{SO}_3\uparrow$$

The stability of the oxysalts is governed, to a large extent, by the radius of the ions present. Thus, when cupric carbonate (small cation, large anion) is heated and loses carbon dioxide to form cupric oxide (smaller anion), the increase in electrostatic attraction in passing from the carbonate to the oxide is considerable. But in going from, say, potassium carbonate (large cation) to potassium oxide, the gain in electrostatic attraction is *relatively* much less, and decomposition will not occur.

5.10 GENERATION OF AN ELECTRIC CURRENT BY CHEMICAL ACTION

In a Daniell cell, the reaction taking place is:

$$\mathrm{Zn} + \mathrm{Cu}^{++} \rightarrow \mathrm{Zn}^{++} + \mathrm{Cu} \quad \text{(energy liberated)}$$

The zinc ions are more stable than the cupric ions

$$\mathrm{Cu}^{++} + 2e \rightarrow \mathrm{Cu}$$
$$\mathrm{Zn} - 2e \rightarrow \mathrm{Zn}^{++}$$

When a cell is formed from two metals, as in the above example, the metal higher in the electrochemical series always becomes the negative pole since it reduces ions of the lower metal, itself being oxidized with the liberation of electrons.

The Daniell cell is constructed from a zinc rod immersed in dilute sulphuric acid (or zinc sulphate solution) in a porous pot connected to a copper plate immersed in cupric sulphate solution. The E.M.F. is 1·08 volts.

In the simple cell, plates of copper and zinc are placed in dilute sulphuric acid and connected externally (by wires) to a small lamp, which lights up. The reaction taking place is:

$$\mathrm{Zn} + 2\mathrm{H}^+ \rightarrow \mathrm{Zn}^{++} + \mathrm{H}_2 \qquad \underbrace{\text{(energy liberated)}}_{\text{electrical energy + heat energy + work}}$$

The zinc ions are more stable than the hydrogen ions

$$2\mathrm{H}^+ + 2e \rightarrow 2[\mathrm{H}] \rightarrow \mathrm{H}_2 \quad \text{(at the copper plate)}$$
$$\mathrm{Zn} - 2e \rightarrow \mathrm{Zn}^{++} \quad \text{(at the zinc plate)}$$

Electrons flow from the zinc to the copper through the wires and bulb, while the conventional electric current flows in the opposite direction.

The E.M.F. is about 1 volt, but falls off after the cell has been working for some time owing to a layer of hydrogen bubbles which collect on the copper plate, preventing hydrogen ions from losing their charge and thus setting up a 'back E.M.F.'. This is termed *polarization.* The hydrogen bubbles can be brushed off the copper plate. Also, a commercial zinc rod dissolves in dilute sulphuric acid even when the cell is not in use (called *local action*) and this is overcome by amalgamating the zinc (rubbing it with mercury).

An experiment which can be performed to demonstrate the formation of simple voltaic cells using metals in the electrochemical series is as follows. Seven thin strips of copper are screwed on to one side of a wooden block. Opposite each strip of copper is attached a strip of the following metals: Mg (use magnesium ribbon wound round a thin strip of wood), Al, Zn, Fe, Sn (use tinfoil wound as for magnesium), Pb and Cu. All the strips of metal on the one side, and all on the other, are connected together and then the apparatus is connected to a sensitive voltmeter. If a beaker of dilute sulphuric acid is placed under opposing pairs of metals in turn, a different potential difference will be recorded. Why?

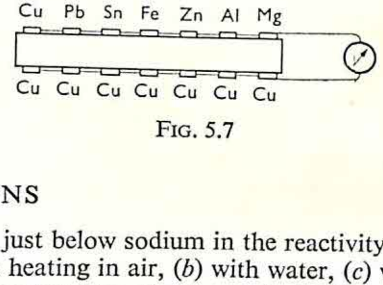


FIG. 5.7

5.11 QUESTIONS

1. Barium comes just below sodium in the reactivity series. Predict its reaction (*a*) on heating in air, (*b*) with water, (*c*) with dilute hydrochloric acid. Predict also the thermal stability of its hydroxide, carbonate and sulphate. Write equations.

2. Cadmium comes just below zinc in the reactivity series. It occurs as a sulphide mineral. How would you expect the metal to be extracted? How would you expect it to react with (*a*) water, (*b*) dilute sulphuric acid?

6 Hydrogen, Acids, Salts

6.1 PREPARATION OF HYDROGEN

In many school laboratories hydrogen is bought contained in steel cylinders. If a preparation is required, it can be made by reduction of hydrogen ions in dilute sulphuric acid by zinc, the reaction being carried out in a Kipp's apparatus (fig. 5.6)

$$Zn + 2H^+ \rightarrow Zn^{++} + H_2\uparrow$$

If pure zinc is used the reaction is very slow but it can be accelerated by addition of a few drops of cupric sulphate solution, a layer of copper being deposited on the zinc. When zinc and copper touch internally in dilute sulphuric acid, a cell called a galvanic (metallic) couple is formed. Hydrogen is liberated at the copper surface.

6.2 OTHER REACTIONS IN WHICH HYDROGEN IS FORMED

(*a*) Reaction of water on certain metals (5.4).

(*b*) Reaction of aluminium, zinc, or tin with sodium hydroxide or potassium hydroxide solution.

$$Zn + 2OH^- \rightarrow \underset{\text{zincate ion}}{ZnO_2^{--}} + H_2\uparrow$$

$$2Al + \underset{\text{(hot, conc.)}}{2OH^-} + 2H_2O \rightarrow \underset{\text{aluminate ion}}{2AlO_2^-} + 3H_2\uparrow$$

$$Sn + \underset{\text{(hot, conc.)}}{2OH^-} + 4H_2O \rightarrow \underset{\text{stannate}}{Sn(OH)_6^{--}} + 2H_2\uparrow$$

Note: Zincate ions can also be represented as $Zn(OH)_4^{--}$ and aluminate ions as $Al(OH)_4^-$.

(*c*) By electrolysis (see 3.4).

6.3 MANUFACTURE OF HYDROGEN

(a) From oil

Methane CH_4, which is the 'natural gas' of petroleum oilfields, is reacted with steam at 900°C in the presence of a nickel catalyst.

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

A similar reaction occurs when methane is partially oxidized by oxygen in the presence of nickel at 900°C.

$$2CH_4 + O_2 \rightarrow 2CO + 4H_2$$

The mixture of gases is passed with steam over a heated catalyst (nickel, 450°C) to give hydrogen and carbon dioxide; the latter is dissolved in water under pressure, for example:

$$\overbrace{CO + 3H_2} + H_2O \rightarrow CO_2 + 4H_2$$

(b) From coal (Bosch process)

Steam is passed over white hot coke to give water-gas (see chap. 10) and the hydrogen is obtained as described in (*a*).

$$C + H_2O \rightarrow \underset{\text{water-gas}}{CO + H_2} \quad \Delta H = +32 \text{ kilocalories (absorbed)}$$

$$\underset{\text{steam}}{H_2O} + \overbrace{CO + H_2} \rightarrow CO_2 + 2H_2$$

6.4 PHYSICAL PROPERTIES OF HYDROGEN

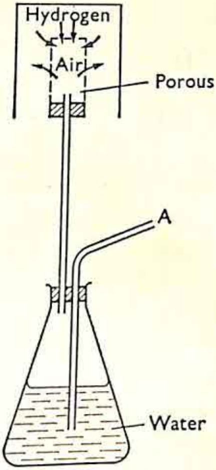


FIG. 6.1

It is a colourless, odourless gas, very sparingly soluble in water, difficult to liquefy and solidify. A soap bubble blown with hydrogen rises, showing that hydrogen is lighter than air.

Another way of showing that hydrogen is lighter than air is by using gaseous diffusion (2.22). The apparatus used is shown in fig. 6.1.

A jet of water is pushed out of the tube at A. This is because hydrogen passes into the porous pot more rapidly than air inside the pot can get out. As a result, there is an increase of pressure inside the pot. [If carbon dioxide (heavier than air) is used instead of hydrogen, the pressure inside the pot is reduced and air is sucked in through A.]

6.5 CHEMICAL PROPERTIES OF HYDROGEN

(a) Reduction of elements by hydrogen

When a mixture of hydrogen and oxygen is sparked, or when a jet of hydrogen is ignited in oxygen (or air), water is formed.

$$2H_2 + O_2 \rightarrow 2H_2O$$

Under certain conditions, the mixture of gases will explode when ignited. If hydrogen is collected in a test-tube, a shrill 'pop' is heard when the gas is ignited (test for hydrogen); the less air present the more muffled the 'pop'.

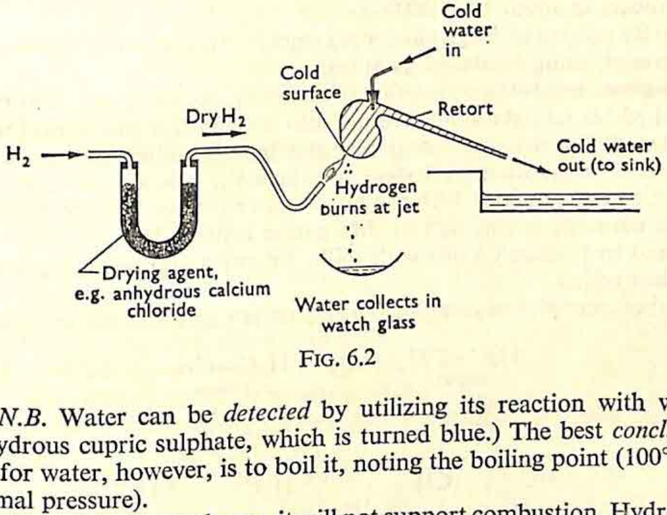


FIG. 6.2

(*N.B.* Water can be *detected* by utilizing its reaction with white anhydrous cupric sulphate, which is turned blue.) The best *conclusive* test for water, however, is to boil it, noting the boiling point (100°C at normal pressure).

Although hydrogen burns, it will not support combustion. Hydrogen reacts with most elements to form compounds called *hydrides*. Thus, water is the hydride of oxygen. Examples of other hydrides are:

sodium hydride	$2Na + H_2 \xrightarrow{\text{heat}} 2Na^+H^-$
calcium hydride	$Ca + H_2 \xrightarrow{\text{heat}} Ca^{++}(H^-)_2$
hydrogen chloride	$H_2 + Cl_2 \rightarrow 2HCl$
hydrogen sulphide	$H_2 + S \xrightarrow{\text{heat}} H_2S$
ammonia	$3H_2 + N_2 \rightleftharpoons 2NH_3$ (see 9.5)
methane	$C + 2H_2 \rightarrow CH_4$ (see 10.4)
acetylene	$2C + H_2 \rightarrow C_2H_2$ (see 10.7)

(b) Reduction of compounds by hydrogen

Hydrogen reduces the basic oxides of metals below zinc in the electrochemical series (see fig. 6.3), for example:

$$Fe_3O_4 + 4H_2 \rightleftharpoons 3Fe + 4H_2O$$
$$PbO + H_2 \rightarrow Pb + H_2O$$
$$CuO + H_2 \rightarrow Cu + H_2O$$

Hydrogen is used in catalytic hydrogenation of unsaturated organic compounds. The ways in which this may be achieved are:

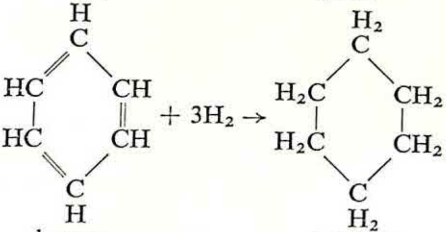
(*a*) By passing hydrogen and vapour of the compound over a catalyst (nickel at about 100°–200°C).

(*b*) By passing hydrogen under pressure into a solution of the organic compound, using a catalyst as in (*a*).

One example is the conversion of naturally occurring oils into more useful edible fats. An oil converted into a fat in this way is said to be 'hardened'. By using different oils and by controlling the hardening process by regulating the extent to which the oils are reduced, it is possible to obtain fats which can be used for as many different purposes as the naturally occurring fats. Margarine is made by mixing fats and oils and hydrogenated oils with milk. Vitamins and colouring matter are then added.

Other examples of catalytic hydrogenation reactions are as follows:

$$\underset{\text{ethylene}}{H_2C{=}CH_2} + H_2 \rightarrow \underset{\text{ethane}}{H_3C{-}CH_3}$$



benzene cyclohexane

Ordinary hydrogen will not reduce well-known salts which are oxidizing agents, e.g. ferric chloride, potassium permanganate, potassium dichromate. If, however, the hydrogen is actually generated within the solution ('nascent' hydrogen) reduction can take place. Thus, if zinc and dilute sulphuric acid are added to a yellow solution of ferric chloride, a green solution of the ferrous salt is formed.

Reduction by nascent hydrogen is very common in organic chemistry.

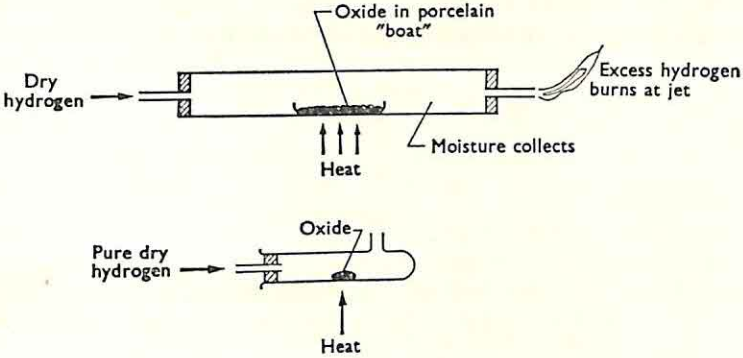


FIG. 6.3

For example, methyl cyanide is reduced to ethylamine by nascent hydrogen produced when sodium reacts with ethanol.

$$2Na + 2C_2H_5OH \rightarrow \underset{\text{sodium ethoxide}}{2C_2H_5O^- + 2Na^+} + 2[H]$$

$$\underset{\text{methyl cyanide}}{CH_3C \equiv N} + 4[H] \rightarrow \underset{\text{ethylamine}}{CH_3.CH_2.NH_2}$$

6.6 USES OF HYDROGEN

(*a*) Making ammonia by the Haber process (see 9.5).

(*b*) Catalytic hydrogenation (see 6.5).

(*c*) Oxy-hydrogen welding.

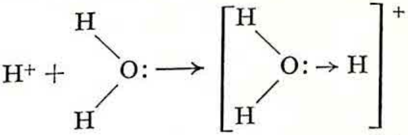
(*d*) Rocket fuel (liquid hydrogen).

(*e*) Industrial preparation of hydrogen chloride and hydrochloric acid (see 13.4).

(*f*) Filling meteorological balloons.

6.7 ACIDS

An acid is a compound which produces hydroxonium ions H_3O^+ (hydrated protons, see 2.9) in aqueous solution and which, under suitable conditions, can yield salts by replacement of all or part of its 'acidic' hydrogen with metallic ions (or ions behaving as such, e.g. NH_4^+).



($\rightarrow$ = co-ordinate or dative covalent linkage)

The *strength* of acids is determined by the relative proportions of hydroxonium ions produced in comparable solutions. *Concentration* is the weight of acid in a given volume of solution. For example, hydrochloric acid is a *strong* acid because it so readily forms hydroxonium ions; but it may be either *dilute* or *concentrated* as may be desired.

General properties of acids

Hydrochloric, sulphuric and nitric acids are obtained from minerals and are therefore called *mineral acids*.

(*a*) Sour taste: the sour taste of many foods is due to acids, e.g. lemons contain citric acid, grapes contain tartaric acid, vinegar contains acetic acid.

(*b*) They are often corrosive, especially when pure or in concentrated solution, e.g. concentrated sulphuric rapidly corrodes paper and skin. Some, however, are not at all corrosive, e.g. carbonic acid, citric acid.

(*c*) They affect indicators. An *indicator* is a substance which, by changing colour, shows whether it is an acidic or alkaline $\left\{\begin{array}{l}\text{solution}\\ \text{medium}\end{array}\right.$ (see 7.5).

Table 6.1

Indicator	*Colour in acid media*	*Colour in alkaline media*
Litmus	Red	Blue
Methyl orange	Red	Yellow
Methyl red	Red	Yellow
Phenolphthalein	Colourless	Pink

(*d*)

$$\underset{\substack{(\text{dil. HCl}\\ \text{dil. } H_2SO_4)}}{\text{Acid}} + \text{metal} \rightarrow \text{salt} + \text{hydrogen}\uparrow$$

i.e. the metal *reduces* hydrogen ions in the acid to hydrogen atoms and is itself oxidized to metal ions, for example:

$$Zn + 2H^+ \rightarrow Zn^{++} + H_2\uparrow$$

(*e*) Acid + metal carbonate → salt + water + carbon dioxide↑

For example:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2\uparrow$$
$$CO_3^{--} + 2H^+ \rightarrow H_2O + CO_2\uparrow$$

Here the weak acid, carbonic acid, is displaced by the stronger one, e.g. hydrochloric acid, and the carbonic acid then decomposes into carbon dioxide and water.

(*f*) Acid + base → salt + water

If the base is also an alkali (see 7.9), the reaction is called a *neutralization*, for example:

$$\text{(i)}\quad \underset{\substack{\text{(or } Cu^{++}O^{--}\text{)} \\ \text{(base, not alkali)}}}{CuO} + 2H^+ \rightarrow Cu^{++} + H_2O$$

$$\text{(ii)}\quad \underset{\substack{\text{sodium hydroxide} \\ \text{(alkali)}}}{\overbrace{Na^+ + OH^-}} + \overbrace{H^+ + Cl^-} \rightarrow \overbrace{Na^+ + Cl^-} + H_2O$$

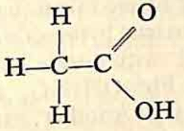
$$\Delta H = -13{\cdot}7 \text{ kilocalories (neutralization)}$$

$$\text{or } OH^- + H^+ \rightarrow H_2O \quad \Delta H = -13{\cdot}7 \text{ kilocalories}$$

The *basicity* of an acid is the number of hydrogen ions (which will then hydrate to form hydroxonium ions) per 'molecule' of the acid. Thus hydrochloric acid is monobasic, sulphuric dibasic and phosphoric acid tribasic.

$$HCl \rightarrow H^+ + Cl^-$$
$$H_2SO_4 \rightarrow 2H^+ + SO_4^{--}$$
$$H_3PO_4 \rightarrow 3H^+ + PO_4^{---}$$

In many cases, the basicity can be deduced merely by inspection of the formula but care should be exercised with organic acids, where not all of the hydrogens in the molecule can exist as hydrogen ions, and will therefore never be replaced, e.g. acetic acid CH_3COOH is monobasic.



$$\rightleftharpoons CH_3COO^- + H^+$$

Hydrogen atoms united directly to a carbon atom do not form hydrogen ions.

For acids with basicities greater than unity, the hydrogen ions can be replaced one at a time, thus leading to the formation of *acid salts*, for example:

sulphuric acid H_2SO_4
↙ ↘
Normal salts — Acid salts
e.g. $(Na^+)_2SO_4^{--}$ — $Na^+HSO_4^-$

A *normal salt* is one formed when all the hydrogen ions of an acid have been replaced by metallic ions (or ions behaving as such).

General ways of making acids

(*a*) Action of water on an acidic oxide (acid anhydride), for example:

$$SO_3 + H_2O \rightarrow H_2SO_4$$

(*b*) Combination of hydrogen with a non-metal and passage of the resulting compound into water, for example:

$$H_2 + Cl_2 \rightarrow \underset{\substack{\downarrow \text{water} \\ \text{hydrochloric acid}}}{2HCl}$$

(*c*) Displacement from a salt by a less volatile acid, for example:

$$Na^+Cl^- + \underset{\text{(conc.)}}{H_2SO_4} \xrightarrow{\text{warm}} Na^+ + HSO_4^- + HCl\uparrow$$

$$Na^+NO_3^- + \underset{\text{(conc.)}}{H_2SO_4} \xrightarrow{\text{warm}} Na^+ + HSO_4^- + HNO_3\uparrow$$

6.8 SALTS

The meaning of the terms *normal salt* and *acid salt* has been given in 6.7. There are several other types of salt.

(a) Basic salts

It can be imagined that some salts are formed from bases. Thus, lead nitrate $Pb^{++}(NO_3^-)_2$ can be derived from lead hydroxide $Pb^{++}(OH^-)_2$ by replacement of two hydroxide ions OH^- with nitrate ions NO_3^-. If only one OH^- ion is replaced, a basic salt $Pb^{++}OH^-NO_3^-$ is formed. This can be written as $Pb(NO_3)_2.Pb(OH)_2$. Another example is basic cupric sulphate $xCuSO_4.yCu(OH)_2$ (where x and y are small whole numbers).

(b) Double salts

These are formed when solutions containing equi-formula weight quantities of simple salts are mixed and the solution crystallized, e.g. cupric ammonium sulphate $CuSO_4.(NH_4)_2SO_4.6H_2O$, ferrous ammonium sulphate $FeSO_4.(NH_4)_2SO_4.6H_2O$, Carnallite $KCl.MgCl_2.6H_2O$, and Dolomite $MgCO_3.CaCO_3$.

(c) Complex salts

These contain one or more complex ions. These are formed by the co-ordination (see 2.9) of an ion by one or more *ligands* (groups which can form a co-ordinate covalent bond with the ion; they can be either ions, atoms or molecules).

1. Cationic complex ions bear a positive charge, for example:

cuprammonium ion $[Cu(NH_3)_4]^{++}$, deep blue
hydrated cupric ion $[Cu(H_2O)_4]^{++}$, light blue

2. Anionic complex ions bear a negative charge, for example:

ferrocyanide ion $[Fe(CN)_6]^{----}$
ferricyanide ions $[Fe(CN)_6]^{---}$

An example of a complex salt is cuprammonium sulphate $[Cu(NH_3)_4]^{++}SO_4^{--}.H_2O$, formed by adding alcohol to the deep blue solution obtained when excess ammonia solution is added to cupric sulphate solution (deep blue crystals separate out).

N.B. (*a*) The colours of aqueous solutions of salts are typical of their characteristic hydrated ions (ions co-ordinated by water molecules).

Hydrated ions have the following colours: Mg^{++}, Ca^{++}, Na^+, K^+, Al^{+++}, Zn^{++}, Sn^{++}, Pb^{++} ions are colourless, Fe^{++} ions are green, Fe^{+++} ions are yellow, Ni^{++} ions are green, Co^{++} ions are pink, Cu^{++} ions are pale blue, etc. In general, ions of transition elements are coloured in aqueous solution (see 2.12).

(*b*) Although sodium, potassium salts, etc. are generally colourless, they will be coloured if the anion is coloured, e.g. sodium dichromate is orange.

(*c*) All common salts of Na^+, K^+, NH_4^+ are soluble in water.

(*d*) All common metallic nitrates are soluble in water.

(*e*) All common metallic chlorides (except those of silver, lead, mercurous and cuprous ions) are soluble in water.

(*f*) All common metallic carbonates (except those of sodium, potassium and ammonium ions) are sparingly soluble in water.

(*g*) All common metallic sulphates (except those of lead, barium and (in concentrated solution) calcium ions) are soluble in water.

(*h*) *Salts do not exist in solution, where the separate ions are present. The salt is formed only when the solution is evaporated and crystallized or evaporated to dryness.*

Deliquescence and efflorescence

In some cases, hydrated salts lose their water of crystallization (either entirely or in part) simply on exposure to the atmosphere at normal temperatures. This phenomenon is called *efflorescence*. Examples are $Na_2CO_3 . 10H_2O$ (goes to the monohydrate) and $Na_2SO_4 . 10H_2O$ (goes to the anhydrous salt).

Sometimes, salt hydrates absorb so much water on exposure to the atmosphere that they form saturated solutions, this being called *deliquescence*. Examples are calcium chloride $CaCl_2 . 6H_2O$, magnesium chloride $MgCl_2 . 6H_2O$, and also phosphorus pentoxide P_2O_5 and sodium hydroxide NaOH (these are not salts).

In efflorescence, the vapour pressure of the hydrated salt is greater than the vapour pressure of water vapour in the atmosphere. The salt tries to equalize pressures but, in view of the size of the atmosphere, this can never be achieved and so it passes to a lower hydrate or the anhydrous salt, with a lower vapour pressure.

In deliquescence, the vapour of the salt hydrate (and its saturated solution) is less than the vapour pressure of water vapour in the atmosphere. The salt tries to equalize pressures by absorbing water from the atmosphere, forming eventually an unsaturated solution.

It should be remembered that the water vapour present in the atmosphere is not constant, varying from day to day and *especially* from summer to winter. Hence, there is a possibility that certain compounds may be either efflorescent or deliquescent depending on the season or the locality.

A *hygroscopic* substance (e.g. conc. H_2SO_4, CuO) absorbs water from the atmosphere without forming a solution.

General methods for preparing salts

Remember that salts do not exist in solution, only the separate *ions* being present, and that the salt only turns up when the solution is evaporated.

(*a*) Action of an acid on a metal, for example:

$$Zn + 2H^+ + SO_4^{--} \rightarrow \underbrace{Zn^{++} + SO_4^{--}}_{ZnSO_4} + H_2\uparrow$$

or

$$Zn - 2e \rightarrow Zn^{++}$$
$$2H^+ + 2e \rightarrow H_2$$

Add excess metal to the (warm) acid, filter when reaction is complete, evaporate the filtrate and allow to crystallize. Rinse the crystals with pure solvent and dry them carefully.

(*b*) Reaction of an acid on an insoluble base, for example:

$$\underset{(\text{or } Cu^{++}O^{--})}{CuO} + 2H^+ + SO_4^{--} \rightarrow \underbrace{Cu^{++} + SO_4^{--}}_{CuSO_4} + H_2O$$

Add excess base to the (hot) acid, filter, evaporate the filtrate, and allow to crystallize.

(*c*) Reaction of an acid on a soluble oxide, hydroxide or carbonate. An indicator is used to show when excess of the base or carbonate has been added. The colour of the indicator can be removed by boiling the solution with animal charcoal.

(*d*) Sparingly soluble salts can be prepared by precipitation, for example:

$$\overbrace{Ag^+ + NO_3^-} + \overbrace{H^+ + Cl^-} \rightarrow AgCl\downarrow + \overbrace{H^+ + NO_3^-}$$

$$\overbrace{Pb^{++} + 2NO_3^-} + \overbrace{2H^+ + SO_4^{--}} \rightarrow PbSO_4\downarrow + \overbrace{2H^+ + 2NO_3^-}$$

The solid is filtered off, washed and dried.

(*e*) By direct synthesis (building up) from the elements, for example:

$$2Al + 3Cl_2 \xrightarrow{\text{heat}} 2AlCl_3 \quad (\text{or } Al_2Cl_6)$$

$$2Fe + 3Cl_2 \xrightarrow{\text{heat}} 2FeCl_3 \quad (\text{or } Fe_2Cl_6)$$

$$2Ag + Cl_2 \xrightarrow{\text{heat}} 2Ag^+Cl^-$$

$$2Na + Cl_2 \xrightarrow{\text{heat}} 2Na^+Cl^-$$

6.9 QUESTIONS

1. Write notes on the following:
  (*a*) the preparation of hydrogen,
  (*b*) the manufacture of hydrogen,
  (*c*) an experiment to show that hydrogen is lighter than air,
  (*d*) the uses of hydrogen,
  (*e*) nascent hydrogen.

2. Define the term 'acid'. What are the general properties of acids?

3. Give an account of the classification of salts. Describe the preparation of pure specimens of (*a*) zinc sulphate from zinc, (*b*) cupric sulphate from cupric oxide, (*c*) lead chloride from lead nitrate.

7 Oxygen and its Compounds

7.1 PREPARATION OF OXYGEN

Oxygen is normally obtained from a cylinder when required, but it is often convenient to prepare some in order to see where it comes from. The most convenient method is from hydrogen peroxide solution, which is cheap, easily handled, and available from the local pharmacist. Two methods of generation are possible:

(*a*) Warming the solution

$$2H_2O_2 \rightarrow 2H_2O + O_2\uparrow$$

(*b*) Catalytic decomposition of the solution using manganese dioxide at room temperature.

Another method of preparation, not so good because the material is uncommon and difficult to keep, is from sodium peroxide $(Na^+)_2O_2^{--}$, which is reacted with water at room temperature.

$$O_2^{--} + 2H_2O \rightarrow 2OH^- + H_2O_2 : 2H_2O_2 \rightarrow 2H_2O + O_2\uparrow$$

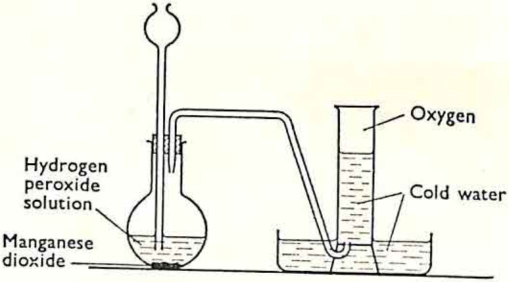


FIG. 7.1

7.2 OTHER REACTIONS IN WHICH OXYGEN IS FORMED

(*a*) Heat on mercuric or silver oxide, for example:

$$2HgO \rightarrow 2Hg + O_2\uparrow \quad \text{(Priestley's method, 1774)}$$

(*b*) Heat on potassium chlorate with a cupric oxide, nickel oxide (or manganese dioxide) catalyst.

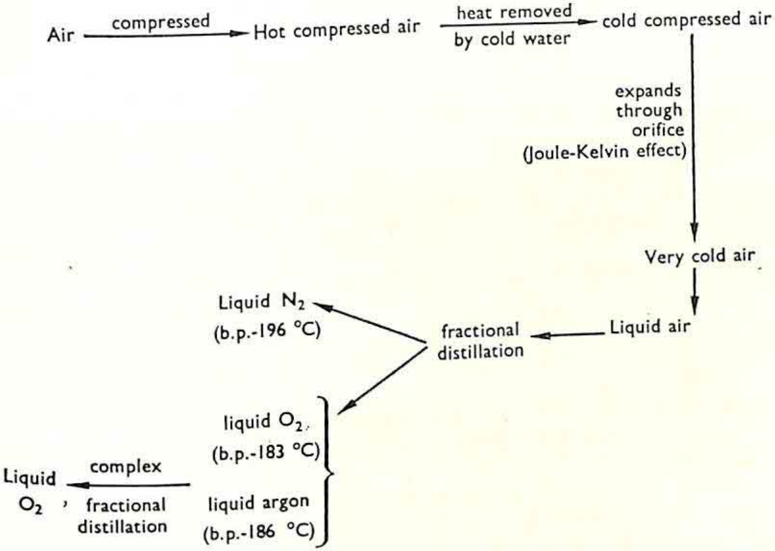
$$2KClO_3 \rightarrow 2KCl + 3O_2\uparrow$$

(*c*) Electrolysis of dilute sulphuric acid (3.4).
(*d*) Heat on nitrates.
(*e*) Photosynthesis (feeding of plants).

$$\text{carbon dioxide} + \text{water} + \text{sunlight energy} \xrightarrow{\text{chlorophyll}} \underset{\text{sugars}}{\text{starches}} + \text{oxygen}\uparrow$$

7.3 MANUFACTURE OF OXYGEN

Fractional distillation of liquid air.



7.4 PHYSICAL PROPERTIES OF OXYGEN

Oxygen is a colourless, odourless gas which has about the same density as air. It is slightly soluble in water (fishes breathe dissolved oxygen). It is very difficult to liquefy and solidify.

7.5 CHEMICAL PROPERTIES OF OXYGEN

(*a*) It supports life.
(*b*) It is a good oxidizer (4.1) and can oxidize both elements and compounds. It supports combustion, e.g. a glowing splint which is rekindled (test for oxygen).

Oxygen oxidizes elements forming oxides. It oxidizes metals, the ease decreasing with decreasing position in the electrochemical series, for example:

$$2Ca - 4e \rightarrow 2Ca^{++}$$
$$O_2 \rightarrow 2[O], \qquad 2[O] + 4e \rightarrow 2O^{--}$$
$$2Ca^{++} + 2O^{--} \rightarrow 2Ca^{++}O^{--}$$

Oxides of metals are generally basic oxides (bases), these being oxides which react with acids to form salts plus water only, for example:

$$Ca^{++}O^{--} + \overbrace{2H^{+} + 2Cl^{-}} \rightarrow \overbrace{Ca^{++} + 2Cl^{-}} + H_2O$$

Oxygen also oxidizes many non-metals to oxides, e.g. hydrogen to water H_2O, sulphur to sulphur dioxide SO_2 (and sulphur trioxide SO_3), carbon to carbon dioxide CO_2 (and carbon monoxide CO), phosphorus to phosphorus pentoxide P_2O_5 (and phosphorus trioxide P_2O_3), nitrogen to nitric oxide NO, xenon to xenon trioxide XeO_3, etc.

Non-metals normally form acidic oxides, although water, nitrous oxide and nitric oxide are neutral. Acidic oxides are oxides which react with bases to give SALTS plus water only, and often react directly with water to give acids, for example:

$$SO_2 + \overbrace{2Na^{+} + 2OH^{-}} \rightarrow \overbrace{2Na^{+} + SO_3^{--}} + H_2O$$
$$SO_2 + H_2O \rightarrow 2H^{+} + SO_3^{--} \quad \text{(sulphurous acid)}$$

Xenon oxide is unusual in that it gives a (slightly) acidic solution but, with alkalis, the solution decomposes into xenon and a xenate (e.g. $(Na^{+})_4XeO_6^{----}$).

When an acidic oxide reacts directly with water to form an acid it is called an *acid anhydride* (see 6.8), e.g. SO_2 is the anhydride of sulphurous acid H_2SO_3, SO_3 is the anhydride of sulphuric acid H_2SO_4, CO_2 is the anhydride of carbonic acid H_2CO_3, CO is the anhydride of formic acid ($HCOOH$), etc.

Oxygen can also oxidize compounds, e.g. sulphur dioxide to sulphur trioxide

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \qquad \Delta H = -45 \text{ kilocalories (liberated)}$$

nitric oxide to nitrogen dioxide

$$2NO + O_2 \rightleftharpoons 2NO_2$$

phosphorus trioxide to phosphorus pentoxide

$$P_2O_3 + O_2 \rightarrow P_2O_5$$

barium oxide to barium peroxide

$$2BaO + O_2 \rightleftharpoons 2BaO_2$$

ammonia to nitrogen

$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$ (oxidation by removal of hydrogen)

methane to carbon dioxide

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

7.6 USES OF OXYGEN

(*a*) In making steel.
(*b*) In welding: a blowpipe is used.

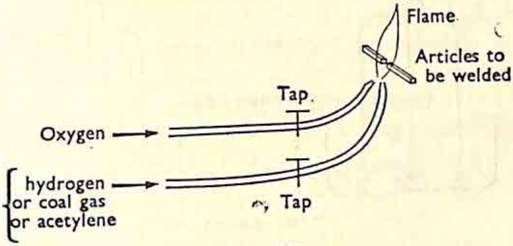


FIG. 7.2

Flames produced have temperatures of approximately 3200°C (oxy-acetylene), 2800°C (oxy-hydrogen) and 2500°C (oxy-coal gas).

(*c*) Breathing where oxygen is scarce, e.g. high altitude flying, deep sea diving, mountaineering, hospitals (oxygen-tents), etc.

7.7 COMBUSTION AND THE COMPOSITION OF THE AIR

The earliest theories were based on the phlogiston concept (Becher and Stahl, about 1700).

Substance burns → Phlogiston + Calx (ash)

This was overthrown by the work of Priestley (discovery of oxygen) and Lavoisier (work on combustion), 1774.

Lavoisier heated mercury in a vessel connected to a bell-jar containing air inverted over a trough of mercury. The mercury developed a coating of red mercuric oxide and the level of mercury in the bell-jar

Lavoisier's experiment

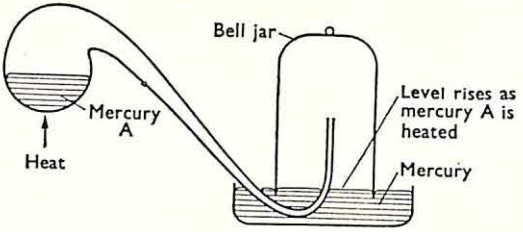


FIG. 7.3

Bell-jar experiment

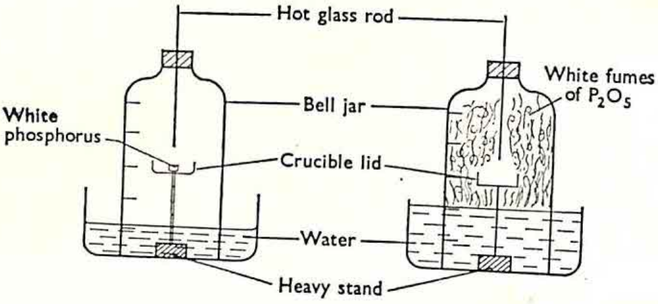


FIG. 7.4

Rusting

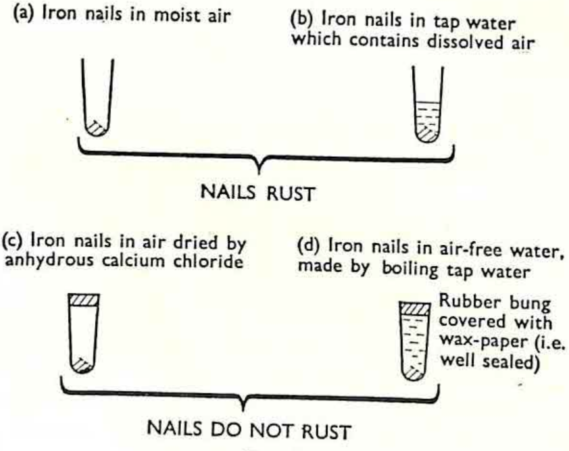

(a) Iron nails in moist air
(b) Iron nails in tap water which contains dissolved air
NAILS RUST
(c) Iron nails in air dried by anhydrous calcium chloride
(d) Iron nails in air-free water, made by boiling tap water
Rubber bung covered with wax-paper (i.e. well sealed)
NAILS DO NOT RUST

FIG. 7.5

rose, showing that some of the air (about one-fifth by volume) was used during combustion. A similar experiment can be performed in the laboratory using the apparatus shown in fig. 7.4.

This experiment shows that about one-fifth of the air is oxygen. It can also be done using a candle, or by using the process of *rusting*. Rust is formed when iron is exposed to the action of both air and water, the rust being hydrated ferric oxide, $Fe_2O_3.H_2O$ or $FeO.OH$. It is possible to show that both oxygen and water are needed using the conditions shown in fig. 7.5.

Iron can be protected from rusting by coating it with grease, paint, plastic or a metal (e.g. zinc, tin, chromium). When covered with zinc, the iron is said to be galvanized. This is better than tinning since zinc lies above iron in the electrochemical series while tin lies below it. In a solution of an electrolyte (ordinary water contains traces of electrolytes such as carbonic acid), zinc ions would tend to be formed rather than ferrous ions leaving the iron surface, if the protective coating is scratched. Hence, rusting cannot occur readily. For tinned iron, however, ferrous ions would leave the iron surface more readily than stannous ions would leave the tin surface, making rusting easy.

$$Fe \rightarrow Fe^{++} + 2e, \qquad Fe^{++} \xrightarrow{\text{air}} Fe^{+++} \xrightarrow[\text{rust}]{H_2O} FeO.OH$$

In order to utilize rusting in the elucidation of the composition of the atmosphere, the apparatus of fig. 7.6 is employed.

Composition of the air by rusting

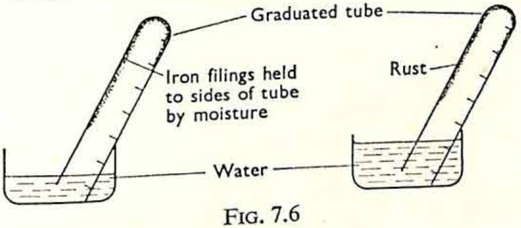


FIG. 7.6

The inside of a long glass tube is damped with water and iron filings sprinkled in, where they stick to the side of the tube. The tube is inverted over a container of water and left for some time, when it is found that water has risen up inside the tube. After adjusting the levels of water inside and outside the tube to be equal, it is found that approximately one-fifth of the air inside the tube has been used up in rusting, i.e. one-fifth of the air (by volume) is oxygen.

7.8 BREATHING (RESPIRATION)

The essential equation is

$$C + O_2 \rightarrow CO_2 \qquad \Delta H = -94{\cdot}5 \text{ kilocalories (liberated)}$$

Oxygen is inhaled, combines with haemoglobin in the blood to form oxy-haemoglobin which is circulated around the body, and is given up to various carbon compounds (from food) with the liberation of carbon dioxide and heat.

Inhaled air	*Exhaled air*
(*a*) Nitrogen 80% approx.	(*a*) Nitrogen 80% approx.
(*b*) Oxygen 20% approx.	(*b*) Oxygen 16% approx.
(*c*) Carbon dioxide 0·03% approx.	(*c*) Carbon dioxide 4% approx. (this percentage is not, in fact, quite the same as the percentage of oxygen used up).
	(*d*) Water vapour (more than inhaled).

To show that more carbon dioxide is present in exhaled air than in inhaled air, the apparatus of fig. 7.7 is used.

Breathing experiment

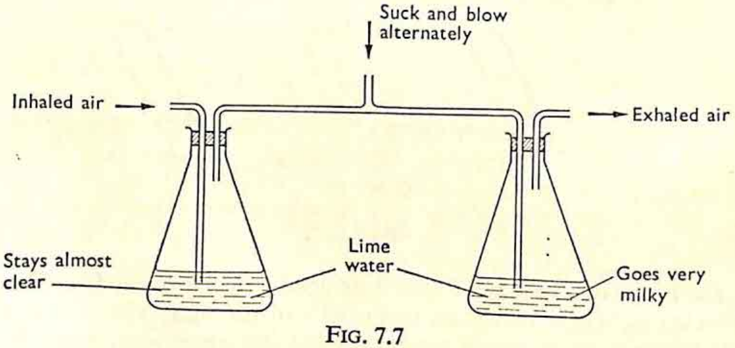


FIG. 7.7

The heat energy released in respiration is used (*a*) for warmth, (*b*) for work and play, (*c*) to provide energy so that other changes in the body, which need energy before they can take place, can be started.

7.9 OXIDES

Oxides can be either electrovalent, e.g. $(Na^+)_2O^{--}$ or covalent, e.g. CO_2.

(*a*) Acidic oxides are those which react with bases to form a salt plus water only, e.g. CO_2, SO_2, SO_3, P_2O_5, N_2O_5

$$CO_2 + 2OH^- \rightarrow CO_3^{--} + H_2O$$
$$CO_3^{--} + H_2O + CO_2 \rightarrow 2HCO_3^-$$

With water, they give acids, for example:

$$CO_2 + H_2O \rightarrow 2H^+ + CO_3^{--}$$
$$SO_3 + H_2O \rightarrow 2H^+ + SO_4^{--}$$

They are generally the oxides of non metals, but there are exceptions, for example:

$$\underset{\substack{\text{chromic}\\ \text{anhydride}}}{CrO_3} + H_2O \rightarrow \underset{\text{chromic acid}}{\overbrace{2H^+ + CrO_4^{--}}}$$

$$\underset{\substack{\text{manganese}\\ \text{heptoxide}\\ \text{(very explosive)}}}{Mn_2O_7} + H_2O \rightarrow \underset{\text{permanganic acid}}{\overbrace{2H^+ + 2MnO_4^-}}$$

(*b*) Basic oxides (or bases) are those which react with acids to give salts plus water only, for example:

$$Cu^{++}O^{--} + \overbrace{2H^+ + 2Cl^-} \rightarrow \overbrace{Cu^{++} + 2Cl^-} + H_2O$$

Bases which dissolve in water give *alkaline* solutions, containing *alkalis*, e.g. sodium oxide $(Na^+)_2O^{--}$ dissolves in water to form sodium hydroxide (caustic soda) Na^+OH^-, potassium oxide $(K^+)_2O^{--}$ gives potassium hydroxide (caustic potash) K^+OH^-, calcium oxide $Ca^{++}O^{--}$ gives calcium hydroxide $Ca^{++}(OH^-)_2$.

A strict definition of a *base* is a substance with a tendency to accept a proton (cf. an *acid* is a substance which donates a proton), for example:

$$\underset{\text{base}}{NH_3} + H^+ \rightarrow NH_4^+$$

$$\underset{\text{base}}{OH^-} + H^+ \rightarrow H_2O$$

$$\underset{\text{base}}{H_2O} + H^+ \rightarrow H_3O^+$$

Notice that water can act as either an acid or a base.

$$H_2O \rightleftharpoons H^+ + OH^- \quad \text{(acidic function)}$$
$$H_2O + H^+ \rightarrow H_3O^+ \quad \text{(basic function)}$$

(*c*) Amphoteric oxides have both basic and acidic characteristics, reacting with acids to give salts plus water and with alkalis to give salts plus water, for example

$$ZnO + 2H^+ \rightarrow Zn^{++} + H_2O \quad \text{(zinc salt)}$$
$$ZnO + 2OH^- \rightarrow ZnO_2^{2-} + H_2O \quad \text{(zincate)}$$
$$Al_2O_3 + 6H^+ \rightarrow 2Al^{+++} + 3H_2O \quad \text{(aluminium salt)}$$
$$Al_2O_3 + 2OH^- \rightarrow 2AlO_2^- + H_2O \quad \text{(aluminate)}$$

(*d*) Neutral oxides are neither acidic, basic nor amphoteric, e.g. water H_2O, nitrous oxide N_2O, nitric oxide NO.

(*e*) Peroxides react with ice-cold water or dilute mineral acids to give hydrogen peroxide, e.g. $(Na^+)_2O_2^{--}$, $Ba^{++}O_2^{--}$.

$$O_2^{2-} + 2H_2O \rightarrow 2OH^- + H_2O_2$$
$$BaO_2 + H_2SO_4 \rightarrow BaSO_4\downarrow + H_2O_2$$
$$2O_2^- + 2H_2O \rightarrow 2OH^- + H_2O_2 + O_2\uparrow$$

(*f*) Higher oxides contain the element in a valency state higher than its normal value, but do not give hydrogen peroxide with water or dilute acids, e.g. the metallic dioxides (containing high percentages of covalent bonding) MnO_2, PbO_2.

Note that *higher oxides*, when heated with concentrated hydrochloric acid, give chlorine, whilst peroxides give hydrogen peroxide with the cold acid (if hot, oxygen is evolved).

(*g*) Mixed oxides behave as though they are mixtures of two simple oxides, e.g. N_2O_4 (behaves as N_2O_3 and N_2O_5), red lead Pb_3O_4 (PbO_2, $2PbO$), Fe_3O_4 (FeO, Fe_2O_3). [There is really more to it than this, however, as, for example, Pb_3O_4 can be treated as plumbous plumbate $(Pb^{2+})_2(PbO_4)^{4-}$.]

Along a Period of the Periodic Table, there is a gradual change in nature of the 'typical' oxides (i.e. the ones in which the element exerts the Group valency). For example: *Period* 2

$$\begin{array}{ccccccc} (Na^+)_2O^{--} & Mg^{++}O^{--} & Al_2O_3 & SiO_2 & P_2O_5 & SO_3 & Cl_2O_7 \\ & & & & (P_4O_{10}) & & \end{array}$$

$$\longleftarrow \text{Basic} \longrightarrow \ \text{Amphoteric} \longleftarrow \text{Acidic} \longrightarrow$$

The same gradation is found in lower Periods, if the transition series are neglected.

7.10 HYDROXIDES OF METALS

These are closely related to the corresponding oxides.

Preparation

1. Reaction of a metal with water (5.4).
2. Reaction of a metallic oxide with water, this applying to the oxides of sodium, potassium, calcium and (to a lesser extent) magnesium.

$$O^{--} + H_2O \rightarrow 2OH^-$$

3. Electrolysis, e.g. the Castner-Kellner cell (fig. 3.8).
4. By precipitation (for insoluble ones), for example:

$$\begin{gathered}Pb^{++} + 2OH^- \rightarrow Pb(OH)_2\downarrow \quad \text{(white)}\\ Cu^{++} + 2OH^- \rightarrow Cu(OH)_2\downarrow \quad \text{(blue)}\\ Fe^{++} + 2OH^- \rightarrow Fe(OH)_2\downarrow \quad \text{(green)}\\ Fe^{+++} + 3OH^- \rightarrow Fe(OH)_3\downarrow \quad \text{(red/brown)}\\ Al^{+++} + 3OH^- \rightarrow Al(OH)_3\downarrow \quad \text{(white)}\\ Zn^{++} + 2OH^- \rightarrow Zn(OH)_2\downarrow \quad \text{(white)}\end{gathered}$$

Some hydroxides are amphoteric—they dissolve in excess sodium hydroxide solution as well as in acids, for example:

$$Al(OH)_3 + Na^+ + OH^- \rightarrow \underbrace{\overbrace{Na^+ + AlO_2^-}}_{\text{sodium aluminate}} + 2H_2O$$

$$Zn(OH)_2 + 2Na^+ + 2OH^- \rightarrow \underbrace{\overbrace{2Na^+ + ZnO_2^{2-}}}_{\text{sodium zincate}} + 2H_2O$$

Other metallic hydroxides dissolve in excess ammonia solution forming complex ions (6.8). Thus, cupric hydroxide and zinc hydroxide dissolve to form deep blue and colourless solutions respectively, containing the ions $Cu(NH_3)_4^{++}$ or $Zn(NH_3)_4^{++}$ respectively.

Properties

1. Metallic hydroxides are basic, reacting with acids to give salts plus water only, for example:

$$Mg^{++}(OH^-)_2 + 2H^+ \rightarrow Mg^{++} + 2H_2O$$

or

$$OH^- + H^+ \rightarrow H_2O$$

2. When metallic hydroxides are soluble in water they are called alkalis, e.g. NaOH, KOH, $Ca(OH)_2$. Ammonia solution, loosely called

Table 7.1

Metal	*Formula of hydroxide*	*Preparation*	*Colour*	*Solubility in H_2O*	*Heat*	*Acid*	*Alkali*
K	KOH	H_2O on metal or oxide, or electrolysis of solution of a salt	White	soluble ↓ alkaline solutions	melt, no decomposition	Give salts plus water only	
Na	NaOH						
Ca	$Ca(OH)_2$				stability decreases ↓ oxide+ water formed		
Mg	$Mg(OH)_2$	NaOH solution or ammonia solution on a solution of a metallic salt		slightly soluble			
Al	$Al(OH)_3$			only sparingly soluble			Amphoteric
Zn	$Zn(OH)_2$						
Fe	$Fe(OH)_2$, $Fe(OH)_3$		Ferrous—Green Ferric—Brown				
Sn	$Sn(OH)_2$		White				Amphoteric
Pb	$Pb(OH)_2$						
Cu	$Cu(OH)_2$		Blue				
Hg	None						
Ag							

ammonium hydroxide and represented NH_4OH, has many of the general characteristics of alkalis, although it does not contain a metallic ion. Ammonium hydroxide has never been isolated.

3. The effect of heat on metallic hydroxides is given in 5.8.

4. All bases react with most ammonium salts when heated to give ammonia, for example:

$$2NH_4^+Cl^- + \overbrace{Ca^{++} + 2OH^-} \rightarrow 2NH_3\uparrow + \overbrace{Ca^{++} + 2Cl^-} + 2H_2O$$

7.11 WATER

Water is the oxide of hydrogen, H_2O. It is such an excellent solvent that it seldom occurs pure. Sea water contains about 3·6 per cent by weight of dissolved solids, of which about 2·5 per cent is sodium chloride. Rain water and river water are generally much purer.

Water, at 1 atmosphere, boils at 100°C and freezes at 0°C. The presence of dissolved solids raises the boiling point and lowers the freezing point.

Water reacts with many metals (5.4) and with many non-metals, for example:

$$\underset{\text{white hot}}{C} + \underset{\text{steam}}{H_2O} \rightarrow \underset{\text{water gas}}{\overbrace{CO + H_2}} \quad \Delta H = +32 \text{ kilocalories (absorbed)}$$

$$\underset{\text{hot}}{Si} + \underset{\text{steam}}{2H_2O} \rightarrow SiO_2 + 2H_2$$

$$2F_2 + 2H_2O \rightarrow O_2 + \overbrace{4H^+ + 4F^-}$$

$$Cl_2 + H_2O \rightarrow \overbrace{H^+ + Cl^-} + \underset{\text{hypochlorous acid}}{\overbrace{H^+ + OCl^-}}$$

Water also reacts with many compounds, e.g. calcium carbide (to give acetylene), aluminium carbide (to give methane), sodium hydride (to give hydrogen), ethyl acetate (in the presence of an acid or an alkali, to give ethanol and acetic acid or an acetate), acetyl chloride (to give acetic acid). The last two reactions belong to a general class known as *hydrolysis* reactions (for organic compounds), the functional group (see 10.3) of the compound being replaced by the hydroxyl group OH.

$$Ca^{++}(C \equiv C)^{--} + 2H_2O \rightarrow C_2H_2\uparrow + Ca^{++} + 2OH^-$$

$$Al_4C_3 + 12H_2O \rightarrow 3CH_4\uparrow + 4Al(OH)_3$$

$$Na^+H^- + H_2O \rightarrow H_2\uparrow + Na^+ + OH^-$$

$$\underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O \rightleftharpoons \underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{ethanol}}{C_2H_5OH}$$

$$\underset{\text{acetyl chloride}}{CH_3COCl} + H_2O \rightarrow CH_3COOH + HCl$$

The term hydrolysis is also used to represent certain types of reaction in inorganic chemistry, e.g. the reaction of water with certain salts. Thus, an aqueous solution of ferric chloride is acidic to litmus owing to hydrolysis to hydrochloric acid.

$$Fe^{+++} + 3Cl^- + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+ + 3Cl^-$$

The reaction of water with white anhydrous cupric sulphate to give the blue pentahydrate is used as a test for water in liquids.

$$\underset{\text{white}}{CuSO_4} + 5H_2O \rightleftharpoons \underset{\text{blue}}{CuSO_4.5H_2O}$$

Hardness of water

Hard water does not readily give a lather with soap. Hardness is caused by dissolved salts of calcium and magnesium (the sulphates and bicarbonates being most common) which provide Ca^{++} and Mg^{++} ions IN SOLUTION. Thus calcium sulphate occurs as Gypsum (the dihydrate) and, when rain water flows over Gypsum rocks, some of the sulphate is dissolved out. Calcium bicarbonate is formed when rain water (a dilute solution of carbonic acid) flows over calcium carbonate rocks (e.g. limestone).

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{++} + 2HCO_3^-$$

Soap is the sodium or potassium salt of a higher carboxylic acid, stearic acid $C_{17}H_{35}COOH$. Calcium and magnesium ions in water react with soap to give a scum, thereby preventing a lather from forming.

$$2C_{17}H_{35}COO^-Na^+ + Ca^{++} \rightarrow \underset{\substack{\text{scum of calcium}\\\text{stearate}}}{(C_{17}H_{35}COO^-)_2Ca^{++}\downarrow} + 2Na^+$$

Hardness is therefore a nuisance in, for example, laundries.

The volume of standard soap solution required to give a permanent lather with equal volumes of various samples of water can be used to compare their hardness. The relative hardness is expressed as the 'degree of hardness', where 1 degree of hardness is that formed by the presence of 1 part by weight of calcium carbonate (or its equivalent) in 100,000 parts by weight of water. The degree of hardness can be estimated by titration (see 17.3) of a definite volume of the water with a soap solution standardized against water containing a known concentration of Ca^{++} ions.

A better way of estimating hardness in water is with a standard solution of the substance 'complexone' (ethylenediamine tetra-acetic acid, EDTA). This substance forms very stable co-ordinate linkages (see 2.9) with many metal ions, including Ca^{++} and Mg^{++}. The water is first titrated in the presence of a dye called 'solochrome black' which gives a red colour in the presence of Ca^{++} and Mg^{++} ions. At the end-point (when all Ca^{++} and Mg^{++} ions have formed complexes with EDTA), the colour changes from red to blue (the colour of the free solochrome black). Another portion of the water is then titrated in the presence of another dye, called 'murexide', this forming a pink colour with Ca^{++} ions only, when all the latter have formed complexes with EDTA, the free murexide (violet) is liberated.

From the titration results, it is possible to calculate the concentrations of both the Ca^{++} and Mg^{++} ions separately.

The presence of calcium and magnesium bicarbonates causes hardness which is said to be temporary because it can be removed by boiling.

$$Ca(HCO_3)_2 \xrightarrow{\text{boil}} CaCO_3\downarrow + H_2O + CO_2\uparrow$$

Kettle fur and boiler 'scale' are a deposit of calcium carbonate.

Hardness caused by calcium and magnesium sulphates is said to be permanent, since it cannot be removed by boiling.

Softening and deionizing of water

Both temporary and permanent hardness can be removed by the following methods:

1. Use of 'washing soda', sodium carbonate decahydrate $Na_2CO_3.10H_2O$, for example:

$$Ca^{++} + 2Na^+ + CO_3^{--} \rightarrow Ca^{++}CO_3^{--}\downarrow + 2Na^+$$

2. Use of Permutit, an insoluble complex compound (a zeolite) of sodium, which can replace unwanted Ca^{++} and Mg^{++} ions in water by Na^+ ions. The ions are said to be *exchanged* for Ca^{++} and Mg^{++} ions in solution, for example:

$$Ca^{++} + \underset{\text{insol.}}{2Na^+\text{ complex}} \rightarrow \underset{\text{insol.}}{Ca^{++}\text{ complex}} + 2Na^+$$

The water is passed through a container of Permutit, which eventually becomes converted entirely into the calcium complex. This can be 'regenerated' by passing concentrated brine NaCl through it for some time and then washing away the calcium chloride formed.

$$Ca^{++}\text{ complex} + 2Na^+ + 2Cl^- \rightarrow 2Na^+\text{ complex} + Ca^{++} + 2Cl^-$$

3. By use of ion-exchange resins. Permutit softens water by removing calcium and magnesium ions, but it also puts an equivalent quantity of sodium ions into the water. In many branches of science, it is necessary to have water completely free of all ions except H^+ and OH^-. A cation-exchange resin in the form of beads is capable of exchanging cations in the water for H^+ ions (i.e. all unwanted cations are removed and an equivalent number of H^+ ions enter the water), whereas an anion-exchange resin in the form of beads is capable of exchanging anions in the water for OH^- (i.e. unwanted anions are removed and an equivalent number of OH^- ions enter the water). Hence, the only ions present in the water are H^+ and OH^-.

Deionization of water

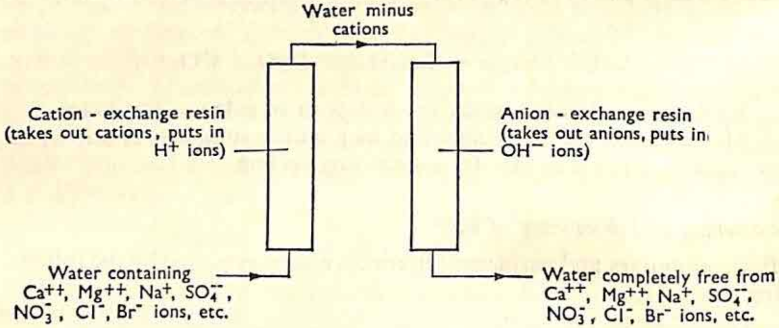

Water minus cations
Cation - exchange resin (takes out cations, puts in H^+ ions)
Anion - exchange resin (takes out anions, puts in OH^- ions)
Water containing Ca^{++}, Mg^{++}, Na^+, SO_4^{--}, NO_3^-, Cl^-, Br^- ions, etc.
Water completely free from Ca^{++}, Mg^{++}, Na^+, SO_4^{--}, NO_3^-, Cl^-, Br^- ions, etc.

FIG. 7.8

4. Distillation, but this is very uneconomical; it is, nevertheless, often used on a large scale.

The following methods can be used for temporary hardness only.

5. Boiling, for example:

$$Ca^{++} + 2HCO_3^- \rightarrow Ca^{++}CO_3^{--}\downarrow + H_2O + CO_2\uparrow$$

6. Use of slaked lime $Ca(OH)_2$ in the calculated quantity, for example:

$$Ca^{++} + 2HCO_3^- + Ca(OH)_2 \rightarrow 2Ca^{++}CO_3^{--}\downarrow + 2H_2O$$

A *detergent* is a cleansing agent, soap being the commonest one. Modern detergents such as Surf, Omo, Daz, Tide are better than soap for the following reasons: they dissolve more readily, they form no scum (soap forms a scum of calcium stearate, but the calcium salts of these detergents are soluble) they work well in both acid and alkaline media, they remove grease efficiently and allow the water to flow more freely through the article being cleansed. Many detergents are products of the petroleum industry.

A solid detergent (sodium dodecyl sulphate) can be made on a small scale by making up a solution of sodium hydroxide (1 g/25 cm^3 of H_2O), adding dodecyl sulphate solution until the solution is neutral and evaporating the solution to dryness on a steam-bath. The solid detergent can be crystallized from dilute ethanol.

STALACTITES AND STALAGMITES

Water containing dissolved calcium bicarbonate can lose water and carbon dioxide by slow evaporation to give calcium carbonate. If this happens on the roof of a cave, a stalac*tite* is formed. If some of the water drips on to the floor and loses carbon dioxide and water there, a stalag*mite* is formed.

Gravimetric composition of water

Dumas's method (1842): laboratory modification.

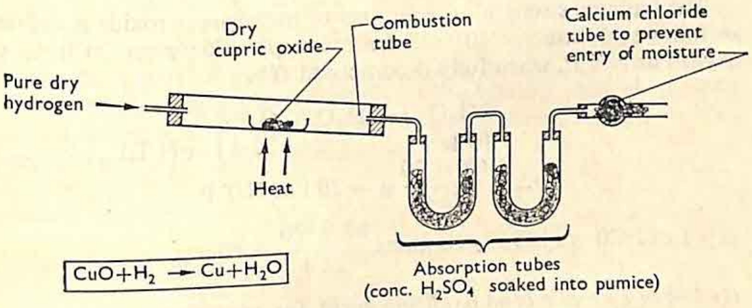

Dry cupric oxide
Combustion tube
Calcium chloride tube to prevent entry of moisture
Pure dry hydrogen
Heat
$\boxed{CuO + H_2 \rightarrow Cu + H_2O}$
Absorption tubes (conc. H_2SO_4 soaked into pumice)

FIG. 7.9

Loss in weight of the cupric oxide gives the weight of oxygen in the water formed. Gain in weight of the absorption tubes gives the weight of water formed.

The difference in these two weights gives the weight of hydrogen in the water. The weight ratio of hydrogen to oxygen is about 1 to 8, the ratio of their equivalent weights.

7.12 HYDROGEN PEROXIDE H_2O_2

This is prepared by reacting a peroxide with an ice-cold dilute mineral acid, for example:

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4\downarrow + H_2O_2$$

or

$$O_2^{--} + 2H^+ \rightarrow H_2O_2$$

It is manufactured by the electrolysis of concentrated sulphuric acid (lead cathode, platinum anode, high current density).

$$2HSO_4^- - 2e \rightarrow H_2S_2O_8 \quad \text{(perdisulphuric acid)}$$

$$H_2S_2O_8 + \underset{\text{steam}}{H_2O} \rightarrow H_2SO_4 + H_2SO_5 \quad \text{(permonosulphuric acid)}$$

$$H_2SO_5 + \underset{\text{steam}}{H_2O} \rightarrow H_2O_2 + H_2SO_4$$

It is a colourless liquid with physical properties different from those of water. It is slightly acidic when pure but the aqueous solution is neutral. The solution decomposes slowly on standing, this being catalysed by finely-divided metals (e.g. platinum), metallic oxides (e.g. MnO_2), dust and alkalis. The pure liquid can decompose violently.

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

The 'volume strength' of solutions of hydrogen peroxide is defined as follows: 1 litre of '20 vol.' hydrogen peroxide gives 20 litres of oxygen at N.T.P. when fully decomposed. Thus:

$$2H_2O_2 \rightarrow 2H_2O + O_2\uparrow$$

$$68\text{ g} \rightarrow \qquad 22{\cdot}4\text{ l at N.T.P.}$$

$$\therefore \quad \frac{68 \times 20}{22{\cdot}4}\text{ g} \rightarrow 20\text{ l at N.T.P.}$$

$$\therefore \quad 1\text{ l of '20 vol.' } H_2O_2 \text{ contains } \frac{68 \times 20}{22{\cdot}4} = \underline{60{\cdot}8\text{ g.}}$$

Hydrogen peroxide is an oxidizing agent, for example:

$$2Fe^{++} + H_2O_2 + \underset{\text{acid}}{\overset{\text{from an}}{2H^+}} \rightarrow 2Fe^{+++} + 2H_2O$$

(observe green solution → yellow)

$$2I^- + H_2O_2 + \underset{\text{acid}}{\overset{\text{from an}}{2H^+}} \rightarrow I_2 + 2H_2O$$

(observe colourless solution → brown)

$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$$

(observe black PbS → white $PbSO_4$)

$$\underset{\text{dichromate ion}}{Cr_2O_7^{2-}} + \underset{\text{from an acid}}{2H^+} + 4H_2O_2 \rightarrow \underset{\text{blue chromium peroxide}}{2CrO_5} + 5H_2O$$

(observe orange solution → blue)

The oxidizing properties make hydrogen peroxide solution a useful mouth gargle, for dressing wounds and cuts, and also a bleaching agent for hair, silk, etc.

Pure hydrogen peroxide (or highly concentrated solution) is used, together with oil, as an under-water fuel. The fuel is ignited by inducing the *exothermic* decomposition reaction by spraying it with a finely-divided solid catalyst. Mixtures of hydrogen peroxide and hydrazine (N_2H_4) are used in rocket propulsion.

Hydrogen peroxide is also a reducing agent, for example:

$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{++} + 8H_2O + 5O_2$$

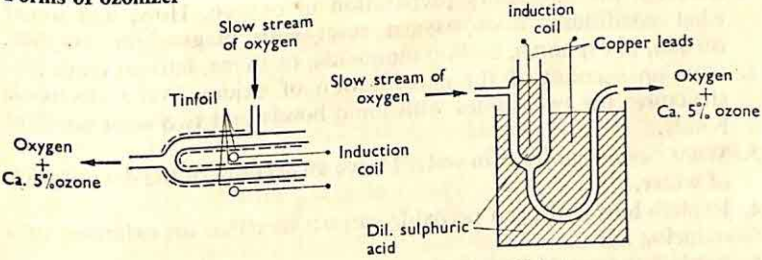
7.13 OZONE O_3

Ozone is an allotrope of oxygen (see 8.2). It is obtained by passing a silent electrical discharge through dry air or oxygen. The silent discharge does not allow the temperature to rise appreciably and the ozone formed does not therefore decompose, as would happen with an ordinary spark.

$$3O_2 \rightarrow 2O_3 \quad \Delta H = 69 \text{ kilocalories (absorbed)}$$

Ozone is a pale blue gas which gives a darker blue magnetic liquid. It can be separated from oxygen by fractional distillation (ozone b.p. −112°C, oxygen b.p. −183°C). It is normally used as ozonized oxygen, as made in an ozonizer, and is then a colourless gas. It has a smell somewhat like traces of chlorine.

Forms of ozonizer



(a) Siemens's type

(b) Brodie's type

FIG. 7.10

Since ozone is an endothermic compound (formed with the absorption of energy) it is very unstable and the pure liquid is liable to explode (the molecules are closer together in the liquid than in the gas state and therefore more collisions are likely, making explosion more probable). Ozone is only slightly soluble in water but is readily absorbed by turpentine.

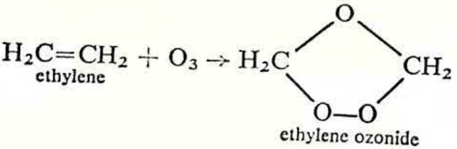
Ozone decomposes into oxygen, decomposition being accelerated by heat and by catalysts.

$$2O_3 \rightarrow 3O_2 \qquad \Delta H = -69 \text{ kilocalories (liberated)}$$

Ozone is a powerful oxidizing agent, for example:

$$2I^- + H_2O + O_3 \rightarrow 2OH^- + I_2 + O_2$$
$$2Fe^{++} + 2H^+ + O_3 \rightarrow 2Fe^{+++} + H_2O + O_2$$
$$PbS + 4O_3 \rightarrow PbSO_4 + 4O_2$$

The 'tailing' of mercury by ozone is an oxidation of the mercury surface. Ozone reacts with unsaturated organic compounds to form ozonides, such as ethylene, benzene, rubber, for example:



Ozone is a useful disinfectant, is used in some air purification plants, and is widely used in organic chemistry for the location of carbon-carbon double and triple bonds.

7.14 QUESTIONS

1. Describe the laboratory preparation of oxygen. How, and under what conditions, does oxygen react with magnesium, sulphur, carbon, phosphorus, carbon monoxide, methane, barium oxide?
2. Give an account of the classification of oxides. Write electronic structures for two oxides with ionic bonds and two with covalent bonds.
3. What causes hardness in water? Give an account of the deionization of water.
4. Explain how hydrogen peroxide can act as either an oxidizing or a reducing agent.
5. Explain the meaning of the term redox, with examples.

8 Sulphur and its Compounds

8.1 OCCURRENCE AND EXTRACTION OF SULPHUR

Sulphur occurs as the element in volcanic regions, e.g. in Sicily near Mount Etna, and also in Texas and Louisiana (U.S.A.). It also occurs as sulphide minerals (see table 5.2).

Sulphur also occurs as metallic sulphates, e.g. Gypsum $CaSO_4.2H_2O$, Anhydrite $CaSO_4$, Epsom salts $MgSO_4.7H_2O$.

Most crude petroleum contains a little sulphur, as does coal.

Sulphur is extracted from the U.S.A. deposits by the Frasch process.

The process relies on the low melting point (119°C) of sulphur. The blasts of hot compressed air (*a*) lower the density of the molten sulphur by making it a froth and (*b*) force it to the surface. On solidification, it forms blocks of sulphur which are recast as sticks of roll sulphur.

The Frasch process

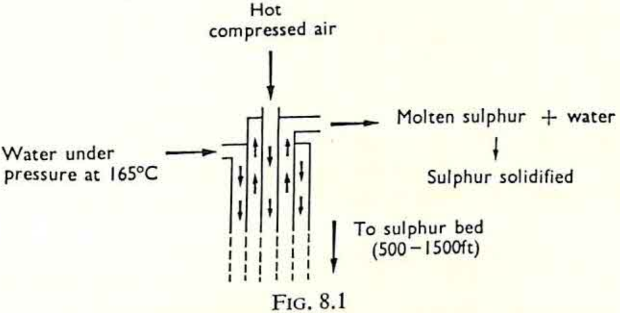


FIG. 8.1

8.2 ALLOTROPY AND PHYSICAL PROPERTIES OF SULPHUR

Allotropy is the existence of an element in two or more forms in the same state of matter. There are several types. Monotropy is when one allotrope is stable and others metastable (theoretically unstable, but in practice reasonably stable), passing at various rates into the stable form. In enantiotropy, each allotrope is stable over a definite range of temperature and passes into another form at the *transition temperature* (point). Enantiotropy is *reversible* whilst monotropy implies non-reversible.

In dynamic allotropy, two allotropes exist in equilibrium together, the percentage of each one being determined by the temperature and sometimes the pressure.

In the solid state, sulphur exhibits enantiotropy, the forms being rhombic ($S\alpha$) and monoclinic or prismatic ($S\beta$) sulphur.

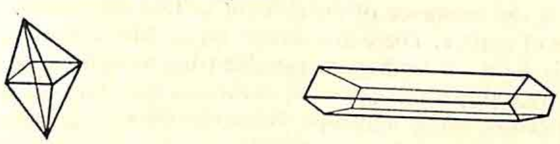
Rhombic sulphur is the common form at normal temperatures. It can be obtained by dissolving powdered roll sulphur in carbon disulphide, filtering and allowing the filtrate to evaporate in the air.

Monoclinic sulphur is stable above 96·5°C to the melting point (119°C). The temperature 96·5°C is the transition point $S\alpha \rightleftharpoons S\beta$. Monoclinic sulphur can be made by (*a*) heating sulphur until it melts to an amber liquid, pouring this into a filter paper and leaving until almost set, and opening the paper quickly, (*b*) dissolving powdered roll sulphur in hot toluene in a tube, wrapping this in cotton wool and allowing it to stand so that crystallization takes place above the transition point, (*c*) melting sulphur in a deep crucible and allowing the melt to cool until a crust forms most of the way over the surface; all the still molten sulphur is then poured away and inside the crucible are found crystals of monoclinic sulphur.

Although the chemical properties of the allotropes are very similar, this is not always true for the allotropes of other elements.

	Rhombic sulphur	*Monoclinic sulphur*
1.	Stable below 96·5°C. Changes slowly to $S\beta$ above this temperature	Stable between 96·5°C and 118·7°C. Changes slowly into $S\alpha$ below this temperature
2.	Octahedral (yellow) crystals	Monoclinic (yellow-brown) needles
3.	Soluble in carbon disulphide, insoluble in water	Same
4.	Density 2·1 g/cm^3	Density 1·995 g/cm^3
5.	M.p. 113·5°C on very slow heating	M.p. 118·7°C

Solid allotropes of sulphur



Rhombic

Monoclinic

FIG. 8.2

When equal weights of the two allotropes are completely burnt in oxygen, the same weight of sulphur dioxide is formed, showing that they are both allotropes of the same element. Also, one form can be converted to the other merely by altering *physical* conditions.

Liquid sulphur contains the dynamic allotropes $S\lambda$ (a clear, yellow, mobile liquid) and $S\mu$ (a dark red, almost black viscous liquid). The percentage of $S\mu$ increases as the temperature rises.

Flowers of sulphur is formed when sulphur vapour falls on a cold surface (sublimation).

Plastic sulphur is formed when boiling sulphur is poured into cold water. It is a rubber-like solid with the same composition as the liquid from which it was derived, i.e. it contains supercooled $S\lambda$ and $S\mu$.

Colloidal sulphur is formed when sodium thiosulphate solution is treated with dilute hydrochloric acid or when hydrogen sulphide solution is oxidized by oxygen.

$$S_2O_3^{--} + 2H^+ \rightarrow SO_2\uparrow + H_2O + S$$
$$2H_2S + O_2 \rightarrow 2H_2O + S$$

Colloidal sulphur is insoluble in carbon disulphide.

Heat on sulphur (in a limited supply of air) (changes due to allotropy)

1. The solid changes from yellow to yellow-brown.
2. It melts to an amber liquid.
3. The liquid darkens and gets more viscous (the tube can be inverted without the liquid running out).
4. The viscosity decreases and the liquid gets even darker, and eventually it boils at 444°C, forming sulphur vapour.

8.3 CHEMICAL PROPERTIES OF SULPHUR

(*a*) Sulphur is oxidized by oxygen, concentrated nitric or hot concentrated sulphuric acid, forming oxides of sulphur; this is oxidation by addition of oxygen atoms.

$$S + O_2 \rightarrow SO_2 \qquad (2S + 3O_2 \rightarrow 2SO_3)$$
$$S + 6HNO_3 \rightarrow SO_3 + 6NO_2\uparrow + 3H_2O : SO_3 + H_2O \rightarrow 2H^+ + SO_4^{--}$$
$$S + 2H_2SO_4 \rightarrow 3SO_2\uparrow + 2H_2O$$

(*b*) Sulphur reacts with most metals (oxidation of the metals), when hot, forming sulphides, for example:

$$Mg + S \rightarrow Mg^{++}S^{--}$$
$$Fe + S \rightarrow Fe^{++}S^{--}$$

The ease of combination decreases with decreasing position of the metal in the electrochemical series.

(*c*) Sulphur also oxidizes many non-metals, when hot, for example:

$$H_2 + S \rightarrow H_2S$$
$$C + 2S \rightarrow CS_2$$

(*d*) Sulphur can also oxidize many compounds, for example:

$$2Na^+ + SO_3^{--} + S \xrightarrow{\text{boil}} 2Na^+ + \underset{\text{sodium thiosulphate}}{S_2O_3^{--}}$$

$$2Na^+ + S^{--} + xS \rightarrow 2Na^+ + \underset{\text{sodium polysulphide}}{[S_x]^{--}} \qquad (x = \text{small whole number})$$

It oxidizes sodium hydroxide solution (conc., hot) to give sodium thiosulphate and sodium polysulphides.

8.4 USES OF SULPHUR

1. Manufacture of sulphuric acid (see 8.8).
2. Manufacture of paper; wood pulp has to be purified by treatment with calcium bisulphite, $Ca(HSO_3)_2$, made from sulphur dioxide (which is made from sulphur). Paper made from pulp not treated in this way soon turns yellow in the light.
3. Vulcanizing rubber; raw rubber is sticky in hot weather and brittle in cold but, by heating the rubber with sulphur, these faults are overcome.
4. Manufacture of gunpowder (sulphur, charcoal, potassium nitrate heated in a confined space form a large volume of gas from a small volume of solid) and matches.
5. Medicinally.
6. Lime-sulphur fungicide and insect killer.
7. Making other important chemicals, e.g. carbon disulphide CS_2, sodium thiosulphate $Na_2S_2O_3$.

8.5 HYDROGEN SULPHIDE H_2S

Preparation

By the action of dilute hydrochloric or dilute sulphuric acid on ferrous sulphide (in a Kipp's apparatus).

$$FeS + 2HCl \rightarrow FeCl_2 + H_2S\uparrow$$

or

$$S^{--} + 2H^+ \rightarrow H_2S\uparrow$$

This reaction involves the displacement of a weak acid (H_2S) by a stronger one (HCl, H_2SO_4), the former being very volatile and having a low solubility in water.

Very pure hydrogen sulphide is obtained when water is added to aluminium sulphide.

$$Al_2S_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2S\uparrow$$

Properties

It is a colourless gas with repulsive smell (bad eggs) and is very poisonous. It is easily liquefied, is fairly soluble in cold water, but less soluble in warm water.

It is a weak dibasic acid in aqueous solution (hydrogen sulphide water).

$$H_2S \rightleftharpoons H^+ + HS^- \rightleftharpoons 2H^+ + S^{--}$$

With sodium hydroxide solution it gives sodium sulphide and sodium hydrosulphide.

$$2OH^- + H_2S \rightarrow S^{--} + 2H_2O$$
$$S^{--} + H_2S \rightarrow 2SH^-$$

It is a reducing agent, e.g. its aqueous solution is slowly oxidized in the air and the gas burns in a limited supply of air.

$$2H_2S + O_2 \rightarrow 2H_2O + 2S\downarrow$$

If burned in a plentiful supply of air, sulphur dioxide is formed.

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$$

It reduces nitric acid of any concentration. A typical equation for the reaction with concentrated nitric acid might be obtained as follows:

(*a*) Hydrogen sulphide in the presence of water is somewhat ionized to give S^{--} ions.

(*b*) Sulphide ions are oxidized to sulphur

$$S^{--} - 2e \rightarrow S$$

(*c*) Nitric acid acts as an oxidizing agent, being itself reduced, for example:

$$4H^+ + 4NO_3^- + 2e \rightarrow 2NO_3^- + 2H_2O + 2NO_2$$
$$\therefore \quad 4H^+ + 2NO_3^- + S^{--} \rightarrow 2H_2O + 2NO_2\uparrow + S$$

It reduces chlorine to hydrogen chloride

$$Cl_2 + H_2S \rightarrow 2HCl + S$$

It reduces potassium permanganate solution (purple) to a solution containing manganous ions (colourless).

$$2MnO_4^- + 6H^+ + 5H_2S \rightarrow 2Mn^{++} + 8H_2O + 5S\downarrow$$

It reduces potassium dichromate solution (orange) to a solution containing chromic ions (green).

$$Cr_2O_7^{--} + 8H^+ + 3H_2S \rightarrow 2Cr^{+++} + 7H_2O + 3S\downarrow$$

It reduces a solution containing ferric ions (yellow) to one containing ferrous ions (green).

$$2Fe^{+++} + H_2S \rightarrow 2Fe^{++} + 2H^+ + S\downarrow$$

It reduces sulphur dioxide (in the presence of moisture) to sulphur.

$$2H_2S + SO_2 \rightarrow 3S\downarrow + 2H_2O$$

Hydrogen sulphide precipitates the sulphides of many metals from solutions containing their ions, for example:

$$Cu^{++} + H_2S \rightarrow \underset{\text{black}}{CuS\downarrow} + 2H^+$$

$$Pb^{++} + H_2S \rightarrow \underset{\text{black}}{PbS\downarrow} + 2H^+$$

The sulphides of tin, lead, bismuth, copper, cadmium, antimony, mercury and silver are precipitated *even* in solution containing dilute hydrochloric acid. The sulphides of zinc, iron, manganese, cobalt and nickel are precipitated *only* in alkaline solution, and are incompletely precipitated in neutral solution.

$$Zn^{++} + H_2S \rightleftharpoons ZnS\downarrow + 2H^+ \qquad (1)$$

The *solubility product*(*s*) of a sparingly soluble electrolyte is defined as the product of the concentrations of the ions (in gram-ions per litre) in a saturated solution of the electrolyte. Thus, for zinc sulphide,

$$S = [Zn^{++}][S^{--}]$$

When the solution is saturated with hydrogen sulphide,

$$H_2S \rightleftharpoons 2H^+ + S^{--} \qquad (2)$$

Zinc sulphide is precipitated by combination of zinc and sulphide ions.

$$Zn^{++} + S^{--} \rightleftharpoons ZnS\downarrow \qquad (3)$$

If hydrogen ions are present (as would be the case when a neutral solution of a zinc salt is used, as shown by equation (1) above), the sulphide ion concentration is lowered, since the product

$$S^1 = [H^+]^2[S^{--}]$$

must remain constant (you can think of this as a sort of solubility product). Hence, precipitation of zinc sulphide is incomplete, since this lowering of the sulphide ion concentration is sufficient to force reaction (3) slightly back to the left. If the solution contained added hydrogen ions, say from dilute sulphuric acid, zinc sulphide would not be precipitated at all, but the small number of hydrogen ions produced in equation (1) merely cause it to be incompletely precipitated. For some sulphides, e.g. cupric sulphide, the solubility product is so low that it is precipitated even when acid is present.

Ammonia solution can be added to neutralize the acidity or ammonium sulphide can be used for the precipitation, for example:

$$Zn^{++} + (NH_4)_2S \rightarrow ZnS\downarrow + 2NH_4^+$$

No sulphides are precipitated for the following metals: potassium, sodium, calcium, magnesium, aluminium, chromium; ammonium sulphide is also soluble in water. Some of these sulphides are stable and soluble; others are unstable and hydrolyse.

Some sulphides are hydrolysed by water, for example:

$$2CaS + 2H_2O \rightarrow Ca^{++} + 2OH^- + Ca^{++} + 2SH^-$$

$$MgS + 2H_2O \rightarrow Mg^{++} + 2OH^- + H_2S\uparrow$$

Most sulphides burn in air to give the oxide and sulphur dioxide, for example:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2\uparrow$$

Test for hydrogen sulphide

It turns lead acetate (or nitrate) paper black, owing to the precipitation of black lead sulphide. The smell is also unmistakable.

8.6 SULPHUR DIOXIDE SO_2

Preparation

It is normally obtained from a cylinder (not the same, though, as for hydrogen, etc); disposable units can now be purchased.

(*a*) By treating a sulphite (or bisulphite or thiosulphate) with dilute hydrochloric acid—displacement of a weak acid by a stronger one (cf. preparation of carbon dioxide). It is soluble in water and heavier than air and is therefore collected by downward delivery.

$$SO_3^{--} + 2H^+ \rightarrow H_2O + SO_2\uparrow$$

(*b*) The reduction of hot concentrated sulphuric acid by copper turnings.

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + 2H_2O + SO_2\uparrow$$

obtained from

$$\begin{array}{l} Cu \rightarrow Cu^{++} + 2e \\ 2H^+ + SO_4^{--} + 2H^+ + 2e \rightarrow 2H_2O + SO_2 \\ \hline Cu + 2H^+ + SO_4^{--} + 2H^+ \rightarrow Cu^{++} + 2H_2O + SO_2\uparrow \\ \hline \end{array}$$

Preparation of sulphur dioxide

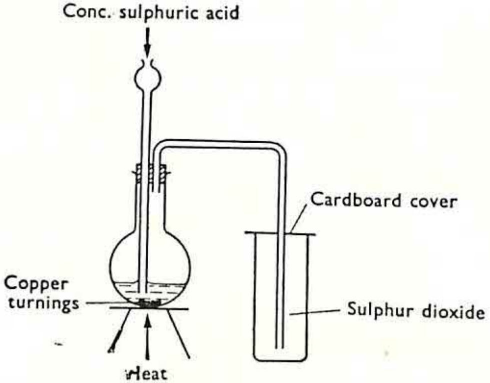


FIG. 8.3

(*c*) It is manufactured by roasting many sulphide minerals in air, e.g. ZnS, or by roasting Anhydrite at 1500°C with coke and sand (see 8.8).

$$2CaSO_4 + C + 2SiO_2 \rightarrow CO_2\uparrow + 2SO_2\uparrow + \underset{\text{calcium silicate}}{2CaSiO_3}$$

Properties

It is a colourless gas with a sharp smell, very easily liquefied, poisonous, and very soluble in water.

With water, sulphurous acid is formed.

$$SO_2 + H_2O \rightarrow 2H^+ + SO_3^{--}$$

With sodium hydroxide solution, a sulphite (excess alkali) and bisulphite (excess sulphur dioxide) are formed.

$$2OH^- + SO_2 \rightarrow SO_3^{--} + H_2O$$
$$SO_3^{--} + SO_2 + H_2O \rightarrow 2HSO_3^-$$

It is a powerful reducing agent, especially in the presence of water.

$$SO_2 + 2H_2O - 2e \rightarrow 4H^+ + SO_4^{--}$$

e.g. when sulphurous acid stands in air, sulphuric acid is slowly formed

$$2H_2SO_3 + O_2 \rightarrow 2H_2SO_4$$

or

$$2SO_3^{--} + O_2 \rightarrow 2SO_4^{--}$$

It reduces concentrated nitric acid to nitrogen dioxide.

$$SO_2 + 2H^+ + 2NO_3^- \rightarrow 2NO_2 + 2H^+ + SO_4^{--}$$

It reduces ferric ions to ferrous ions in aqueous solution (colour change yellow to green).*

$$2Fe^{+++} + SO_3^{--} + H_2O \rightarrow 2Fe^{++} + 2H^+ + SO_4^{--}$$

It reduces chlorine water to hydrochloric acid.

$$Cl_2 + H_2O \rightarrow \overbrace{H^+ + OCl^-} + \overbrace{H^+ + Cl^-}$$

$$\underset{\text{chlorine water}}{\overbrace{H^+ + OCl^- + H^+ + Cl^-}} + SO_3^{--} \rightarrow 2H^+ + 2Cl^- + SO_4^{--}$$

It reduces potassium permanganate solution (purple) to a solution containing manganous ions (colourless).

---

* When the SO_2 is first passed in a red colour (due to complex ions) is produced, the green colour only coming after passing in the gas for some time.

$$2MnO_4^- + 16H^+ + 10e \rightarrow 2Mn^{++} + 8H_2O$$
$$5SO_3^{--} + 5H_2O - 10e \rightarrow 10H^+ + 5SO_4^{--}$$

$$2MnO_4^- + 16H^+ + 5SO_3^{--} + 5H_2O \rightarrow 2Mn^{++} + 8H_2O + 10H^+ + 5SO_4^{--}$$

$$\therefore\ 2MnO_4^- + 6H^+ + 5SO_3^{--} \rightarrow 2Mn^{++} + 3H_2O + 5SO_4^{--}$$

It also reduces sodium dichromate solution (orange) to a solution containing hydrated chromic ions (green).

$$Cr_2O_7^{--} + 14H^+ + 6e \rightarrow 2Cr^{+++} + 7H_2O$$
$$3SO_3^{--} + 3H_2O - 6e \rightarrow 6H^+ + 3SO_4^{--}$$

$$Cr_2O_7^{--} + 14H^+ + 3SO_3^{--} + 3H_2O \rightarrow 2Cr^{+++} + 7H_2O + 6H^+ + 3SO_4^{--}$$

$$\therefore\ Cr_2O_7^{--} + 8H^+ + 3SO_3^{--} \rightarrow 2Cr^{+++} + 4H_2O + 3SO_4^{--}$$

Sulphur dioxide bleaches by reduction, e.g. wool, straw, sponges.

Test for sulphur dioxide

Provided an unknown gas has been shown not to be hydrogen sulphide, the fact that it decolourises potassium permanganate solution and turns potassium dichromate solution green shows that it is sulphur dioxide.

Sulphur dioxide is also an oxidizing agent. For example, it oxidizes hydrogen sulphide to sulphur (in the presence of moisture), burning magnesium to magnesium oxide, and lead dioxide to lead sulphate.

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S$$
$$2Mg + SO_2 \rightarrow 2MgO + S$$
$$PbO_2 + SO_2 \xrightarrow{\text{heat}} PbSO_4$$

Test for sulphite ions

(*a*) Treat the solid substance, or its aqueous solution, with dilute nitric acid and warm gently. Sulphur dioxide is evolved.

(*b*) To a solution of the substance in deionized water, add barium chloride solution. A white precipitate, soluble in dilute hydrochloric acid, confirms a sulphite (provided it is not a soluble carbonate).

Uses of sulphur dioxide

It is used as a bleaching agent, for destroying bacteria and fungi, and as a preservative in fruit juices.

8.7 SULPHUR TRIOXIDE SO_3

Preparation

Sulphur dioxide and oxygen are dried and passed over hot platinized asbestos as shown in fig. 8.4.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \quad \Delta H = -45 \text{ kilocalories (liberated)}$$

Preparation of sulphur trioxide

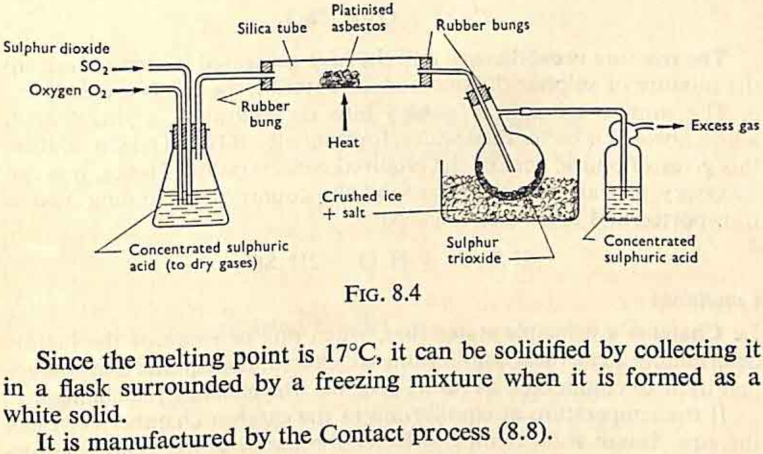


FIG. 8.4

Since the melting point is 17°C, it can be solidified by collecting it in a flask surrounded by a freezing mixture when it is formed as a white solid.

It is manufactured by the Contact process (8.8).

Properties

It is a white solid which exists as needle-shaped crystals. It reacts vigorously with water to give sulphuric acid.

$$SO_3 + H_2O \rightarrow 2H^+ + SO_4^{--}$$

With concentrated sulphuric acid it gives pyrosulphuric acid (fuming sulphuric acid, oleum).

$$SO_3 + \overbrace{2H^+ + SO_4^{--}} \rightarrow \overbrace{2H^+ + S_2O_7^{--}}$$

8.8 SULPHURIC ACID (OIL OF VITRIOL) H_2SO_4

This is manufactured by two processes, the first one being the more important and giving the purer acid.

(a) The Contact process

1. Sulphur dioxide (made by one of the methods given in 8.6) is mixed with air and purified by electrostatic dust precipitation (this involves passing the gases through a chamber in which a central wire electrode is at a very high electrical potential with respect to the other electrode; the dust particles become charged, stick to the electrodes and, on switching off the current, fall to the bottom of the chamber).
2. The mixture is passed over vanadium pentoxide (catalyst) at 450°C.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

The reaction is exothermic and the heat generated is used to heat up the mixture of sulphur dioxide and air entering the catalyst chamber.
3. The sulphur trioxide is passed into concentrated sulphuric acid, which absorbs it better than water, forming oleum $H_2S_2O_7$. On dilution this gives sulphuric acid of the required concentration. Hence, it is not necessary to transport *water* around the country; the fuming acid is transported and diluted as required.

$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$$

Conditions

Le Chatelier's principle states that, when one or more of the factors determining a chemical equilibrium are altered, the equilibrium will adjust itself to counteract, as far as possible, the effect of the changes.

If the temperature at equilibrium in the catalyst chamber is raised, the equilibrium will attempt to lower the temperature. Since the forward reaction is exothermic, this can be achieved by the decomposition of sulphur trioxide into sulphur dioxide and oxygen. Hence, the forward reaction is favoured by low temperatures. In practice, a temperature of 450°C is chosen to give a reasonable rate of reaction and is the optimum working temperature of the catalyst.

Hence, temperature affects (a) *rate of reaction*, (b) *composition of the equilibrium mixture.*

Now let the pressure on the equilibrium be raised. The equilibrium will attempt to lower the pressure. Since pressure is caused by the bombardment of a surface with molecules, and there is a reduction in the number of molecules in passing from left to right, the formation of sulphur trioxide is favoured by high pressures. In practice this is not employed since sulphur dioxide would liquefy at high pressures.

A catalyst speeds up the rates of the forward and reverse reactions to an equal extent, thereby aiding the attainment of equilibrium without affecting its position. Vanadium pentoxide V_2O_5 is chosen in practice.

By the law of mass action (see 16.1), the equilibrium constant is given by the expression:

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

If the maximum yield of sulphur trioxide is to be obtained from a given weight of sulphur dioxide, an excess of air (oxygen) is needed.

(b) The Chamber process

The simplified processes here are as follows:

$$SO_2 + \underset{\text{steam}}{H_2O} + NO_2 \rightarrow H_2SO_4 + NO$$

$$2NO + \underset{\text{air}}{O_2} \rightarrow 2NO_2$$

Intermediate products, notably nitrosyl hydrogen sulphate $NO^+HSO_4^-$, which are sometimes isolated in crystalline form ('Chamber crystals'), have been identified.

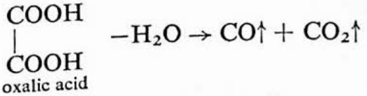
The acid is of about 82 per cent concentration and often contains dissolved oxides of nitrogen, making it valuable for the manufacture of fertilizers.

Properties of sulphuric acid

The concentrated acid is very hygroscopic (hence its use in desiccators). It has a great affinity for water and there is considerable heat evolved when it is added to water. It is used as a dehydrating agent, i.e. it can remove water, or the elements of water, from chemical compounds (cf. drying is the removal of water not in chemical combination), for example:

$$\underset{\text{blue}}{CuSO_4.5H_2O} - 5H_2O \rightarrow \underset{\text{white}}{CuSO_4}$$

$$\underset{\text{formic acid}}{H.COOH} - H_2O \rightarrow \underset{\text{carbon monoxide}}{CO\uparrow}$$



$$\underset{\text{oxalic acid}}{\begin{array}{c} COOH \\ | \\ COOH \end{array}} - H_2O \rightarrow CO\uparrow + CO_2\uparrow$$

(Formates and oxalates also react in a similar manner.)

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} - 11H_2O \rightarrow 12C$$

Hot concentrated sulphuric acid is a powerful oxidizing agent.

$$2H_2SO_4 + 2e \rightarrow SO_4^{--} + SO_2 + 2H_2O$$

For example, with copper turnings

$$Cu - 2e \rightarrow Cu^{++}$$

$$\therefore \quad Cu + \overbrace{2H^+ + SO_4^{--}} + 2H^+ \rightarrow Cu^{++} + SO_2\uparrow + 2H_2O$$

A similar equation is obtained with hot concentrated sulphuric acid on charcoal (carbon).

$$C + 2H_2SO_4 \rightarrow CO_2\uparrow + 2SO_2\uparrow + 2H_2O$$

Dilute sulphuric acid has all the general properties of acids (6.7).

Test for sulphuric acid and the sulphate ion in solution

Add barium chloride and dilute hydrochloric acid (to distinguish from the sulphite ion, barium sulphite being soluble in hydrochloric acid) when a white precipitate of barium sulphate is formed.

$$Ba^{++} + SO_4^{--} \rightarrow BaSO_4\downarrow$$

Sulphuric acid is dibasic and forms two series of salts, the sulphates and bisulphates, for example:

$$(Na^+)_2SO_4^{--},\ Na^+HSO_4^-$$

Uses of sulphuric acid

1. Making fertilizers, e.g. superphosphate

$$\underset{\text{insol.}}{Ca_3(PO_4)_2} + \underset{\text{conc.}}{2H_2SO_4} \xrightarrow{\text{heat}} \underset{\text{soluble calcium dihydrogen phosphate}}{\overbrace{2CaSO_4 + Ca(H_2PO_4)_2}^{\text{superphosphate}}}$$

or
$$2PO_4^{---} + \overbrace{4H^+ + 2SO_4^{--}} \xrightarrow{\text{heat}} \overbrace{2SO_4^{--} + 2H_2PO_4^-}$$

2. Cleaning metal surfaces before coating with a protective metal (the conc. acid is used).

3. Making paints, e.g. the white pigment lithopone, which is a mix-

ture of zinc sulphide and barium sulphate. It is also used to make titanium dioxide, which is a white pigment.

4. In the spinning of cellulose to give rayon.
5. In lead-acid accumulators (contain 1 per cent sulphuric acid).

$$Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O \quad (+ \text{ electrical energy})$$

As the accumulator runs down the specific gravity of the acid decreases from 1·25 to 1·15.

6. In the manufacture of zinc by the electrolytic process.
7. Manufacture of many important sulphates, e.g. $CuSO_4$, $ZnSO_4$, $FeSO_4$, Alums.
8. Removal of impurities from petroleum oil.
9. Manufacture of explosives.

8.9 QUESTIONS

1. Describe the manufacture of sulphur by the Frasch process. How, and under what conditions, does sulphur react with carbon, sodium, sodium hydroxide, sulphuric acid?

2. Explain the meaning of the term allotropy, with reference to sulphur.

3. Give an account of the manufacture of sulphuric acid by the contact method. What factors govern the choice of conditions in this process? Give four uses of sulphuric acid.

4. Give an account of the reducing properties of (*a*) hydrogen sulphide, (*b*) sulphur dioxide. What are the tests for these gases?

9 Nitrogen and its Compounds

9.1 OCCURRENCE

Nitrogen is present in the air (about 80 per cent by volume). It is present, in combination with other elements, in proteins. There is a continual circulation of nitrogen in nature, this being called the nitrogen cycle.

The nitrogen cycle

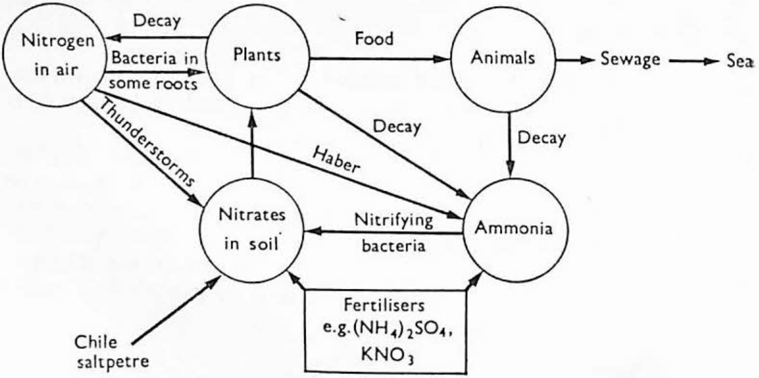


FIG. 9.1

Only relatively few plants (e.g. peas, beans, clover) can take in atmospheric nitrogen directly. All others must absorb it in the form of soluble compounds in the soil. Thunderstorms cause nitrogen and oxygen to combine forming nitric oxide which is oxidized to nitrogen dioxide and dissolved in rain water as very dilute nitric acid. This can react with compounds in the soil to form nitrates.

9.2 PREPARATION OF NITROGEN

Nitrogen is normally obtained from a cylinder.

(a) 'Atmospheric' nitrogen

$$\text{Air} - CO_2 - O_2 \rightarrow \text{'atmospheric' nitrogen}$$

Preparation of 'atmospheric' nitrogen

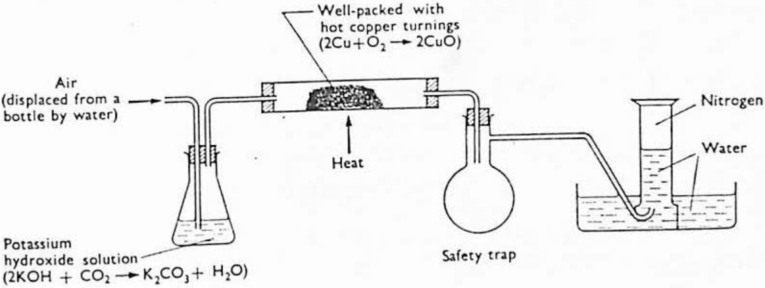

Well-packed with
hot copper turnings
$(2Cu + O_2 \rightarrow 2CuO)$
Air
(displaced from a bottle by water)
Heat
Nitrogen
Water
Potassium
hydroxide solution
$(2KOH + CO_2 \rightarrow K_2CO_3 + H_2O)$
Safety trap

FIG. 9.2

(b) Pure or 'chemical' nitrogen

Heat ammonium nitrite (i.e. a solution containing a mixture of sodium nitrite and ammonium chloride, since ammonium nitrite is so unstable that it cannot be kept).

$$NH_4^+ + NO_2^- \rightarrow N_2\uparrow + 2H_2O$$

Preparation of 'chemical' nitrogen

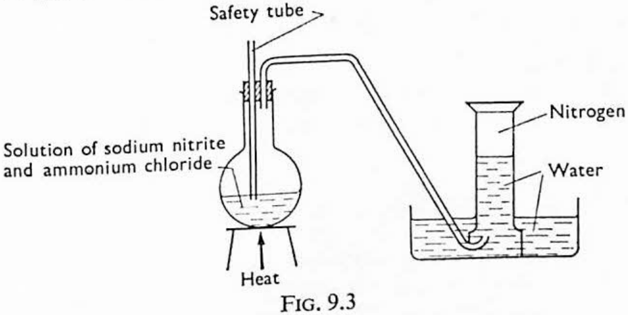


FIG. 9.3

There is a difference in density between atmospheric and chemical nitrogen, and this discovery by Lord Rayleigh (1892) led to the discovery of the Rare Gases. Nitrogen is formed when ammonium dichromate (orange) is heated, a green mass of chromium sesquioxide (chromic oxide) remaining.

$$(NH_4^+)_2Cr_2O_7^{--} \xrightarrow{heat} N_2\uparrow + (Cr^{+++})_2(O^{--})_3 + 4H_2O$$

This reaction cannot be controlled, once started.

A good controllable method is to pass chlorine into EXCESS 0·88 ammonia.

$$8NH_3 + 3Cl_2 \rightarrow N_2 + 6NH_4Cl$$

Yet another method is to pass ammonia over hot cupric oxide.

$$3CuO + 2NH_3 \rightarrow N_2\uparrow + 3Cu + 3H_2O$$

9.3 MANUFACTURE OF NITROGEN

Nitrogen is manufactured by the fractional distillation of liquid air (7.3).

9.4 PROPERTIES OF NITROGEN

It is a colourless, odourless gas, density about the same as that of air, almost insoluble in water (about half as soluble as oxygen). It is very difficult to liquefy.

It is very unreactive. It does not burn and does not support combustion, except in the case of certain metals which form nitrides, for example:

$$3Mg + N_2 \rightarrow \underset{\text{magnesium nitride}}{(Mg^{++})_3(N^{---})_2}$$

Magnesium nitride is one which gives off ammonia when moistened with water and heated.

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3\uparrow$$
$$N^{3-} + 3H_2O \rightarrow 3OH^- + NH_3\uparrow$$

Nitrogen combines with hydrogen to form ammonia (Haber process)

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad \Delta H = -24 \text{ kilocalories (liberated)}$$

The elements are made to combine at 550°C under pressure (200–1000 atm). A catalyst of ferric oxide 'promoted' (or 'activated') by alumina is used. The conditions chosen give the most economical yield of ammonia but all the nitrogen and hydrogen are not used up. The ammonia is liquefied by cooling and unchanged nitrogen and hydrogen recirculated through the plant.

The theoretical conditions can be derived by application of Le Chatelier's principle (cf. 8.8). Let the temperature on the equilibrium mixture be raised. The equilibrium will attempt to lower the temperature. Since the forward reaction is exothermic, the reverse reaction is endothermic and so high temperatures favour the decomposition of ammonia. Hence, the synthesis of ammonia is favoured by low temperatures. In practice, a fairly high temperature is used in order to have a reasonable rate of reaction. Thus, temperature affects (*a*) rate of reaction, (*b*) composition of the equilibrium mixture.

Let the pressure on the equilibrium mixture be raised. The equilibrium will adjust itself to lower the pressure. Since the forward reaction is accompanied by a diminution in the number of molecules, high pressures favour the synthesis of ammonia.

A catalyst is used in order to help the attainment of equilibrium, so that the temperature used to speed up the reaction does not have to be very high (the higher the temperature, the lower the final yield of ammonia).

Nitrogen combines with oxygen at high temperatures to give nitric oxide.

$$N_2 + O_2 \rightleftharpoons 2NO \qquad \Delta H = 43 \text{ kilocalories (absorbed)}$$

9.5 AMMONIA NH_3

Preparation

Ammonia is formed when *any* ammonium salt is warmed with *any* alkali.

$$NH_4^+ + OH^- \rightarrow NH_3\uparrow + H_2O$$

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Preparation of ammonia

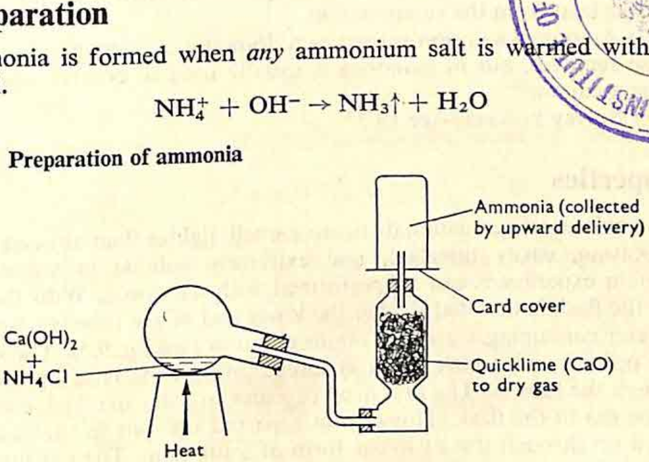

Ammonia (collected by upward delivery)
Card cover
Ca(OH)₂ + NH₄Cl
Quicklime (CaO) to dry gas
Heat

FIG. 9.4

Any alkali can be used owing to the fact that (*a*) the base, ammonia solution, is so weak, (*b*) ammonia is very volatile. Hence, the weak base is displaced by the stronger one.

It cannot be dried by concentrated sulphuric acid or anhydrous calcium chloride, since it reacts with them ($H_2SO_4 \rightarrow$ ammonium sulphate, $CaCl_2 \rightarrow$ a complex, $[Ca(NH_3)_4]^{++}(Cl^-)_2$), but a tower of quicklime is used.

Ammonia can be obtained by heating ammoniacal liquor, obtained at the coal gas works, but this is normally converted directly to ammonium sulphate for use as a fertilizer.

Ammonia is manufactured by the Haber process (9.4).

Uses

(*a*) It is converted to ammonium sulphate for use as a fertilizer.

(*b*) It is converted to nitric acid. Ammonia and air are mixed and passed over a platinum-rhodium catalyst at 920°C forming nitric oxide. This is further oxidized to nitrogen dioxide which is reacted with water in the presence of air to give nitric acid.

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$
$$2NO + O_2 \rightarrow 2NO_2$$
$$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$$

(*c*) Liquid ammonia is used in refrigerators; when it evaporates, it removes heat from the surroundings.

(*d*) Ammonia solution is used as a domestic cleaner; it is used as a grease remover, but in laundries is usually used to control alkalinity of the medium.

(*e*) Solvay process—see 19.3.

Properties

It is a colourless gas with a distinctive smell, lighter than air, can cause suffocation, easily liquefied, and extremely soluble in water; the fountain experiment can be performed with ammonia. With the clip shut the flask is inverted so that the lower end of the tube is immersed in water containing some red litmus solution (see fig. 9.5). The clip is then opened and a little water is forced up into the flask by blowing through the tube A. The first drop of water to enter the flask dissolves all the gas in the flask. This creates a partial vacuum so that water is forced up through the jet in the form of a fountain. The red litmus is turned blue.

In order to prepare ammonia solution, a funnel has to be used to prevent 'sucking back', cf. preparation of hydrogen chloride.

When ammonia dissolves in water, there is a reaction to form an alkaline solution, the high solubility being due to the formation of hydrogen bonds (2.16) between ammonia and water molecules. The net effect is the formation of an entity which is loosely called 'ammonium hydroxide'.

$$NH_3.H_2O \text{ (or } NH_4OH) \rightleftharpoons NH_4^+ + OH^-$$

The 'Fountain' experiment

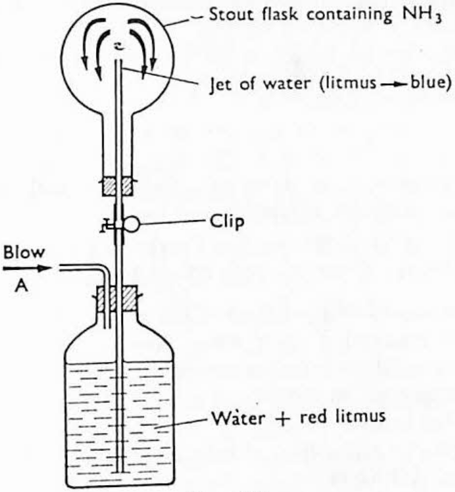


FIG. 9.5

When passed over a hot catalyst ammonia splits up into its elements.

$$2NH_3 \rightarrow N_2 + 3H_2$$

Ammonia is a good *reducing agent.*

(*a*) It does not burn in air but it will burn at a jet in oxygen.

$$4NH_3 + 3O_2 \rightarrow 6H_2O + 2N_2$$

When a mixture of ammonia and oxygen is passed over heated platinum, nitric oxide is formed (see earlier in this section).

(*b*) When ammonia is passed over hot cupric oxide (tube well-packed), nitrogen is formed.

$$3CuO + 2NH_3 \rightarrow N_2\uparrow + 3Cu + 3H_2O$$

(*c*) Ammonia reacts with chlorine as follows.

$$2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl$$

Excess ammonia $NH_3 + HCl \rightarrow NH_4Cl$

Excess chlorine $NH_3 + 3Cl_2 \rightarrow \underset{\substack{\text{nitrogen}\\\text{trichloride}\\\text{(explosive)}}}{NCl_3} + 3HCl$

Test for ammonia

(*a*) Smell
(*b*) Turns moist red litmus blue.
(*c*) Turns Nessler's reagent brown.
(*d*) The blackening of mercurous chloride is a useful qualitative test.

Ammonia solution, and ammonia gas, react with many acids to give ammonium salts, for example:

$$NH_3.H_2O + H^+ + Cl^- \rightarrow NH_4^+ + Cl^- + H_2O$$
$$NH_3 + HCl \rightarrow NH_4Cl \quad \text{(white fumes)}$$

Ammonia solution can precipitate the hydroxides of many metals from solutions containing their ions. Some hydroxides dissolve in excess ammonia solution forming complex ions (see 7.10).

Most common ammonium salts
(*a*) are soluble in water,
(*b*) give ammonia when heated with an alkali,
(*c*) are useful fertilizers,
(*d*) sublime when heated (1.3).

For example, ammonium chloride is a white solid which sublimes on heating, and this can be used to separate it from sodium chloride, which does not sublime.

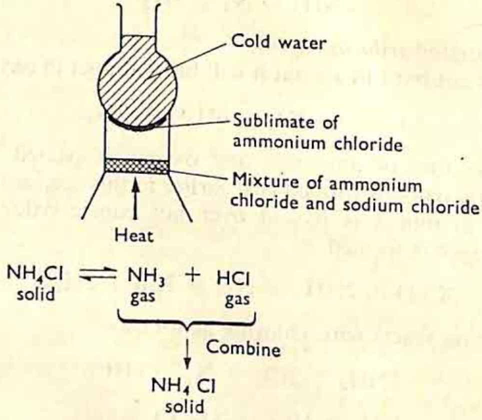

Cold water
Sublimate of ammonium chloride
Mixture of ammonium chloride and sodium chloride
Heat
NH₄Cl solid ⇌ NH₃ gas + HCl gas
Combine
NH₄ Cl solid

FIG. 9.6

It is possible, using the apparatus of fig. 9.7, to show that dissociation occurs when ammonium chloride is heated. This experiment relies on the ability of ammonia to diffuse more rapidly than hydrogen chloride through a small plug of glass wool.

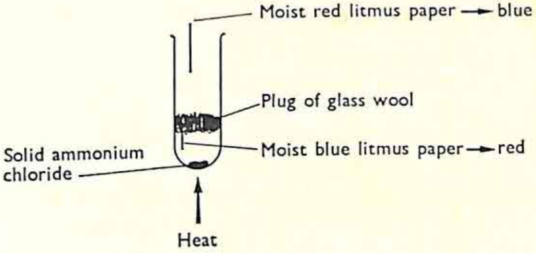


FIG. 9.7

Ammonium chloride is used in dry batteries and in soldering.

Ammonium sulphate is an important fertilizer.

Ammonium nitrate is used in making nitrous oxide and explosives, e.g. amatol is a mixture of T.N.T. and ammonium nitrate in the weight ratio 20 : 80. It is also an important fertilizer.

Ammonium carbonate is present in smelling salts.

Ammonium sulphide is formed when excess ammonia is passed into hydrogen sulphide solution.

$$2NH_3.H_2O + H_2S \rightarrow (NH_4)_2S + 2H_2O$$

It decomposes in air and light.

$$2(NH_4)_2S + 2H_2O + O_2 \rightarrow 4NH_3.H_2O + 2S\downarrow$$

It dissolves sulphur forming yellow ammonium polysulphide $(NH_4)_2S_x$, where x is a small whole number.

9.6 NITROUS OXIDE N_2O

Preparation

Heat on ammonium nitrate (or, better, a mixture of ammonium chloride and sodium nitrate).

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

It is collected over hot water (or dried with concentrated sulphuric acid and collected over mercury).

Preparation of nitrous oxide

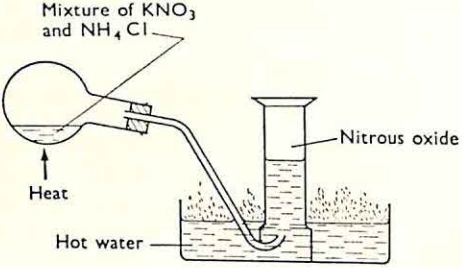


FIG. 9.8

Properties

It is a colourless, sweet-smelling gas, slightly soluble in cold water, but much less soluble in hot water. It is easily liquefied and denser than air. It is used as an anaesthetic in dental and other operations; if administered with oxygen it is very safe and effective.

It sometimes causes hysterical laughter, hence its name 'laughing gas'. It supports combustion of most substances since it decomposes at about 600°C.

$$2N_2O \rightarrow 2N_2 + O_2$$

A glowing splint will cause this decomposition. Other burning elements will continue to burn in it, for example:

$$S + 2N_2O \rightarrow SO_2 + 2N_2$$

It decomposes far more easily than the other oxides of nitrogen (which have a greater proportion of oxygen in them), this being due to the smaller energy barrier (called the energy of activation) opposing its decomposition.

It can be reduced to nitrogen by passage over hot copper or iron.

$$N_2O + Cu \rightarrow CuO + N_2\uparrow$$

Nitrous oxide is a *neutral oxide*.

Distinction from oxygen

Table 9.1

Test	N_2O	O_2
(*a*) Mix with nitric oxide	No reaction	Brown fumes of NO_2
(*b*) Solubility in cold water	Fairly soluble	Almost insoluble
(*c*) Smell	Sweet and sickly	None
(*d*) Pass slowly over hot copper	Nitrogen collected	No gas collected

9.7 NITRIC OXIDE NO

Preparation

(*a*) Half-concentrated nitric acid on copper

$$3Cu + 8HNO_3 \rightarrow 3Cu^{++} + 6NO_3^- + 4H_2O + 2NO\uparrow$$

Preparation of nitric oxide

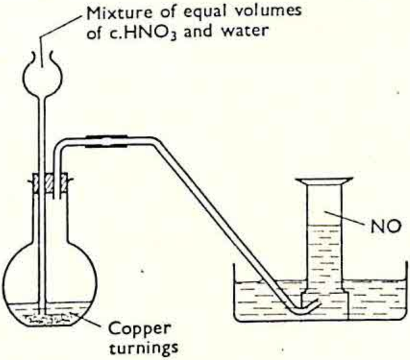


FIG. 9.9

The gas is collected over water, when most of the nitrous oxide and nitrogen dioxide dissolve. To purify it further, it is passed through ferrous sulphate solution to form a brown addition compound, nitrosyl ferrous sulphate $FeSO_4.NO$ (or $[Fe(NO)]^{++}SO_4^{--}$) (the brown ring of the brown ring test). This is heated out of contact with air to give nitric oxide. (Alternatively, the gas can be dried with concentrated sulphuric acid and collected over mercury.)

Properties

It is a colourless gas, density about the same as that of air, and is very sparingly soluble in water.

It turns brown immediately on contact with air or oxygen.

$$2NO + O_2 \rightarrow 2NO_2$$

It does not burn and does not support combustion, except when the substance burns sufficiently vigorously to decompose the gas (about 1000°C).

It is reduced to nitrogen when passed over hot copper or iron.

$$2NO + 2Cu \rightarrow 2CuO + N_2$$

Nitric oxide is a *neutral oxide.*

9.8 NITROGEN DIOXIDE, NO_2, AND DINITROGEN TETROXIDE, N_2O_4

Preparation

(*a*) The action of heat on nitrates of metals below sodium in the electrochemical series.

$$4NO_3^- \rightarrow 4NO_2\uparrow + 2O^{2-} + O_2\uparrow$$

Lead nitrate, $Pb^{++}(NO_3^-)_2$, is generally used since it is always obtained anhydrous; water present would cause the nitrogen dioxide

Preparation of nitrogen dioxide

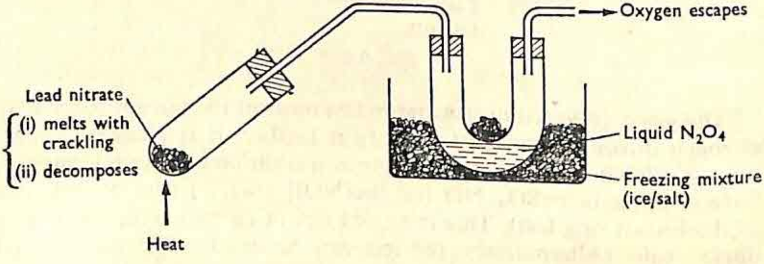


FIG. 9.10

liberated to form nitric acid. When heated, it decrepitates (crackles), brown fumes are seen to be evolved, and a yellow residue (lead monoxide) is formed.

The liquid collected (N_2O_4) should be yellow, but is often green because of traces of nitrogen pentoxide present.

(*b*) Copper and concentrated nitric acid.

$$Cu + 4HNO_3 \rightarrow \overbrace{Cu^{++} + 2NO_3^-} + 2H_2O + 2NO_2\uparrow$$

(*c*) From nitric oxide and oxygen.

Properties

Dinitrogen tetroxide N_2O_4 is a colourless crystalline solid, m.p. $-10°C$.

At 21°C it gives a light brown vapour containing N_2O_4 molecules. On heating, the colour darkens owing to thermal dissociation, this being complete (into NO_2) at about 150°C.

$$N_2O_4 \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} 2NO_2$$

Above this temperature, the colour gets lighter again owing to decomposition of the nitrogen dioxide into nitrogen and oxygen.

A quantitative measure of the extent of dissociation of N_2O_4 into NO_2 at a given temperature can be obtained from a measure of the vapour density (2.22) and the vapour density of undissociated N_2O_4.

Nitrogen dioxide supports combustion of strongly burning substances, e.g. burning magnesium, phosphorus, sulphur. A glowing splint will not decompose it.

It can be reduced to nitrogen by passage over hot copper or iron.

$$2NO_2 + 4Cu \rightarrow 4CuO + N_2$$

Unlike nitrous and nitric oxides, nitrogen dioxide is acidic, being the mixed anhydride of nitrous and nitric acids. The fountain experiment (fig. 9.5) can be performed with it.

$$4NO_2 \equiv \underset{\substack{\text{nitrogen}\\\text{sesquioxide}}}{N_2O_3} + \underset{\substack{\text{nitrogen}\\\text{pentoxide}}}{N_2O_5}$$

Then

$$N_2O_3 + H_2O \rightarrow \underset{\text{nitrous acid}}{2HNO_2}$$

$$N_2O_5 + H_2O \rightarrow \underset{\text{nitric acid}}{2HNO_3}$$

$$\overline{\underline{2NO_2 + H_2O \rightarrow HNO_2 + HNO_3}}$$

With solutions of caustic alkalis, a nitrite and nitrate are formed.

$$2NO_2 + 2OH^- \rightarrow NO_2^- + NO_3^- + H_2O$$

Nitrogen dioxide is very poisonous since it forms nitric acid in the lungs.

$$4NO_2 + 2H_2O + O_2\ (\text{air}) \rightarrow 4HNO_3$$

9.9 NITRIC ACID HNO_3

Manufacture (see 9.5)

Preparation

Nitric acid is made by heating sodium or potassium nitrate with concentrated sulphuric acid, the more volatile acid being displaced.

$$NO_3^- + H_2SO_4 \xrightarrow[\text{(careful)}]{\text{heat}} HSO_4^- + HNO_3\uparrow$$

Preparation of nitric acid

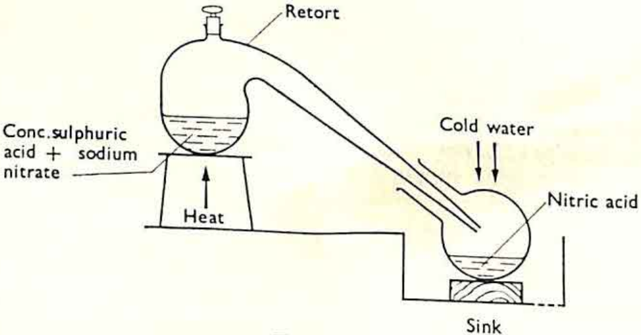


FIG. 9.11

Brown fumes of nitrogen dioxide are seen in the retort owing to decomposition of nitric acid.

$$4HNO_3 \rightarrow 2H_2O + 4NO_2\uparrow + O_2\uparrow$$

Properties

Laboratory concentrated nitric acid has a concentration of about 68 per cent. The pure acid is a colourless, heavy liquid, usually yellow owing to dissolved nitrogen dioxide.

Dilute nitric acid has all the general properties of acids except that it does not give hydrogen with metals (it is a powerful oxidizing agent). It forms salts called the nitrates, and generally oxides of nitrogen are evolved. The concentrated acid renders several metals 'passive', e.g. iron, aluminium (not attacked by acid of concentration greater than 90 per cent).

Nitric acid is a powerful oxidizing agent.

Conc. $2HNO_3 + 2H^+ + 2e \rightarrow 2NO_2 + 2H_2O$

Half-concentrated $HNO_3 + 3H^+ + 3e \rightarrow 2H_2O + NO$

For example:

1. Copper and half concentrated acid (one observes the blue colour of the hydrated cupric ion, and brown fumes of NO_2, formed by reaction of NO evolved with oxygen).

$$\begin{array}{l} 3Cu - 6e \rightarrow 3Cu^{++} \\ 2HNO_3 + 6H^+ + 6e \rightarrow 4H_2O + 2NO \\ \hline 3Cu + 2HNO_3 + 6H^+ \rightarrow 3Cu^{++} + 4H_2O + 2NO \\ \hline \end{array}$$

2. Hydriodic acid (potassium iodide in acid solution) with half-concentrated acid (one observes a change in colour from colourless to brown because of iodine liberated).

$$\begin{array}{l} 6I^- - 6e \rightarrow 3I_2 \\ 2HNO_3 + 6H^+ + 6e \rightarrow 4H_2O + 2NO \\ \hline 6I^- + 2HNO_3 + 6H^+ \rightarrow 3I_2 + 4H_2O + 2NO \\ \hline \end{array}$$

With starch and acidified potassium iodide, one observes a blue colour, due to the complex formed between starch and iodine.

3. Ferrous sulphate in acid solution with half-concentrated acid (one observes a change in colour from green to yellow).

$$\begin{array}{l} 3Fe^{++} - 3e \rightarrow 3Fe^{+++} \\ HNO_3 + 3H^+ + 3e \rightarrow 2H_2O + NO \\ \hline 3Fe^{++} + 3H^+ + HNO_3 \rightarrow 2H_2O + NO + 3Fe^{+++} \\ \hline \end{array}$$

Test for nitric acid and nitrate ions in solution

The Brown ring test: To the solution is added freshly prepared ferrous sulphate solution. The tube is held at about 45° to the horizontal and concentrated sulphuric acid is poured down the inside to form a separate layer at the bottom. A brown ring of $FeSO_4.NO$ where the layers meet indicates the presence of a nitrate.

$$\text{nitrate} + \text{conc. } H_2SO_4 \rightarrow \text{nitric acid } HNO_3$$

$$\text{nitric acid} + \text{ferrous sulphate} \rightarrow \text{ferric sulphate} + \text{water} + NO$$

$$NO + FeSO_4 \rightarrow FeSO_4.NO$$

If the cation associated with the nitrate ion gives an insoluble sulphate, the solution is filtered after addition of ferrous sulphate.

N.B. If a small quantity of a nitrate is warmed with a few cubic centimetres of concentrated sulphuric acid, pale brown fumes of nitrogen dioxide (containing nitric acid vapour) indicates a nitrate. Allow the mixture to cool and add a piece of copper foil. Heat gently; the evolution of deep brown fumes of nitrogen dioxide confirms the presence of a nitrate. [It is assumed that a bromide is absent, otherwise bromine (also brown) is liberated.]

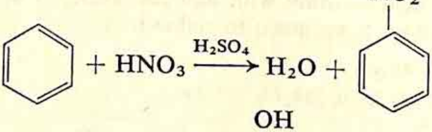
Also, with a nitrate in alkaline solution, ammonia is evolved (quantitatively) by Devarda's alloy (Al, 45; Cu, 50; and Zn 5 per cent). The reaction can be used to estimate the concentration of nitrate ions in a solution, provided no ammonium ions are present.

$$NO_3^- + 4Zn + 7OH^- \rightarrow NH_3\uparrow + 4ZnO_2^{--} + 2H_2O$$

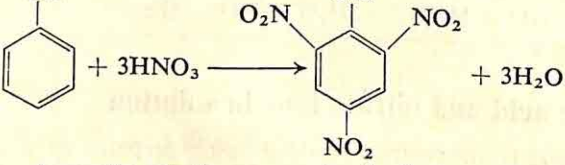
Nitrations

Concentrated nitric acid can nitrate many organic compounds, both aliphatic and aromatic (see 10.3). For example, methane is nitrated in the vapour phase at 500°C, benzene by a mixture of concentrated nitric and sulphuric acids when heated, and phenol by dilute nitric acid at room temperature.

$$CH_4 + HNO_3 \rightarrow CH_3.NO_2 \text{ (nitromethane)}$$



(nitrobenzene)



$+ 3H_2O$ (trinitrophenol)

Aromatic nitration proceeds via the formation of a nitronium ion NO_2^+.

Uses of nitric acid

1. Explosives, e.g. trinitrotoluene T.N.T. $C_6H_2.CH_3(NO_2)_3$, trinitrocellulose (guncotton) $C_6H_7O_2(NO_3)_3$, trinitroglycerine $C_3H_5(NO_3)_3$, dynamite (a mixture of trinitroglycerine and kieselguhr, a form of hydrated silica).
2. Making plastics, e.g. cellulose nitrate fibres; it is also an oxidizing agent in the manufacture of nylon.
3. Making dyestuffs; the azo dyes are derived from aniline $C_6H_5.NH_2$, which is derived from nitrobenzene $C_6H_5.NO_2$.
4. Making fertilizers, e.g. NH_4NO_3, $Ca(NO_3)_2$, Nitrochalk ($NH_4NO_3 + CaCo_3$).

9.10 NITROUS ACID AND NITRITES

Nitrous acid is formed when sodium nitrite reacts with ice-cold dilute hydrochloric or sulphuric acid.

$$NO_2^- + H^+ \rightarrow HNO_2$$

On warming, this decomposes.

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$$

Nitrous acid is both an oxidizing and a reducing agent.

It oxidizes hydrogen sulphide to sulphur.

$$H_2S + 2HNO_2 \rightarrow S + 2H_2O + 2NO\uparrow$$

It oxidizes potassium iodide in acid solution to iodine, and therefore turns starch-iodide paper blue.

$$2NO_2^- + 4H^+ + 2I^- \rightarrow 2NO\uparrow + 2H_2O + I_2$$

It reduces iodine in alkaline solution to iodine ions.

$$I_2 + 2OH^- + NO_2^- \rightarrow 2I^- + NO_3^- + H_2O$$

Test for nitrites

(*a*) If a solid nitrite is treated with dilute hydrochloric acid, nitrogen dioxide fumes (brown) are evolved in the cold.

(*b*) If to a solution containing a nitrite is added freshly prepared ferrous sulphate solution followed by dilute sulphuric acid, a brown colour ($FeSO_4.NO$) is formed.

9.11 QUESTIONS

1. Describe one method by which you could obtain nitrogen (*a*) from the air, (*b*) from a nitrogen compound. What minor constituents would be present in the specimen obtained from the air?

2. What are the uses of nitrogen?

3. Describe how nitrous oxide, nitric oxide and nitrogen dioxide could be obtained from nitric acid. Give a brief account of the properties of these oxides.

4. How may nitrous oxide be distinguished from oxygen?

5. Describe (i) the laboratory preparation and (ii) the manufacture of ammonia. How, and under what conditions, does ammonia react with (*a*) chlorine, (*b*) cupric oxide, (*c*) zinc sulphate, (*d*) cupric sulphate, (*e*) ferrous sulphate, (*f*) oxygen?

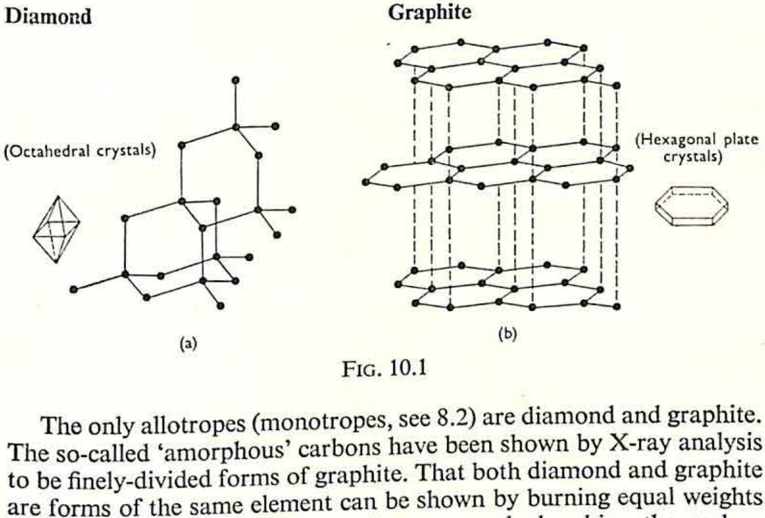
6. Give an account of the nitrogen cycle in nature.

7. How would you show that ammonia is a compound of nitrogen and hydrogen?

10 Carbon and its Compounds

10.1 ALLOTROPY AND PROPERTIES OF CARBON

Carbon occurs free as diamond and graphite. In the combined state it occurs as carbon dioxide CO_2 in the air, as calcium carbonate in chalk, marble and limestone, with hydrogen in natural oils; it is partly free and partly combined in coal.



Diamond

Graphite

(a)

(b)

FIG. 10.1

The only allotropes (monotropes, see 8.2) are diamond and graphite. The so-called 'amorphous' carbons have been shown by X-ray analysis to be finely-divided forms of graphite. That both diamond and graphite are forms of the same element can be shown by burning equal weights of each allotrope in a stream of oxygen and absorbing the carbon dioxide formed in previously weighed bulbs of potassium hydroxide. In each case, the same weight of carbon dioxide is formed.

The crystal structures of diamond and graphite are different (fig. 10.1).

'Amorphous' carbons include:

(*a*) Wood charcoal—made by strongly heating wood in the absence of air; it absorbs gases and is used as a fuel in some countries.

(*b*) Animal charcoal—obtained by heating bones and blood strongly in the absence of air. It contains 10 per cent carbon, the remainder being mainly calcium phosphate. It absorbs colouring matter from solution, e.g. litmus.

(*c*) Lamp black (and soot) is obtained when paraffin, turpentine, etc

Table 10.1

	Diamond	*Graphite*
1.	Occurs naturally (S. Africa)	Occurs naturally (Ceylon)
2.	Made commercially only by heating other forms of carbon under *very* high pressure	Made commercially by Acheson's method, in which coke and sand are heated in an electric furnace $SiO_2 + 3C \rightarrow \underset{\text{silicon carbide*}}{SiC} + 2CO\uparrow$ $SiC \rightarrow Si + C$ (graphite)
3.	Octahedral crystals	Hexagonal crystals
4.	Transparent, sparkle when cut	Grey-black, shiny, opaque
5.	Hard	Softer, greasy
6.	Higher specific gravity	Lower specific gravity
7.	Non-conductor	Conducts both heat and electricity; the weak bonds between sheets of carbon atoms is equivalent to 'spare' electronic charge, making graphite a conductor, since the heat or electric current is carried by the electrons
8.	Burns in air, 900–1000°C	Burns in air, 700°C approx.
9.	Uses include gemstones, cutting tools, rock drillers	Uses include making electrodes, 'lead' pencils, lubricant (the sheets of carbon atoms can slide over one another)

are burnt in a limited supply of air. It is used in black paint and in printer's ink, etc.

(*d*) Sugar charcoal—a very pure form of carbon, made by charring pure sucrose in the absence of air (or with concentrated sulphuric acid).

(*e*) Coke—made by the destructive distillation of coal (see 10.2). It contains about three-quarters of its weight of carbon. It is used in slow combustion stoves and as a reducing agent (e.g. in the iron blast furnace).

(*f*) Gas carbon—obtained as a hard deposit in gas retorts. It conducts electricity and is used in arc lamps.

Coal is an impure form of carbon derived from wood. Wood consists mainly of cellulose and lignin (carbohydrates), the carbon content being about 50 per cent. When wood sank into the Earth in the Carboniferous Age, it became compressed by movement of the Earth's crust, forming coal and other solid fuels. The first stage in this natural modification is peat (used as a fuel and a fertilizer). Next comes lignite (brown coal) which contains about 70 per cent carbon. After this comes the ordinary domestic coal (70–80 per cent carbon) and finally anthracite (smokeless fuel).

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* Called carborundum.

Properties of carbon

1. It burns in a limited supply of air to form carbon monoxide and in a liberal supply of air to form carbon dioxide.

$$2C + O_2 \rightarrow 2CO$$
$$C + O_2 \rightarrow CO_2$$

2. It reduces other elements when hot, e.g. S to give CS_2, F_2 to give CF_4, but not chlorine.

In order to see that this process is reduction, consider that the elements in question, which are all highly electronegative ones, are made up of two parts, (*a*) the electronegative element, (*b*) an electropositive part of zero. When carbon reacts with them, the electropositive part is increased (since carbon is more electropositive than the elements in question) and therefore the elements have been *reduced* (see 4.1).
3. It reduces many compounds when hot, for example:

$$ZnO + C \rightarrow Zn + CO\uparrow$$
$$PbO + C \rightarrow Pb + CO\uparrow$$

In the laboratory, this type of reduction is done on a 'charcoal block', using a mouth blowpipe.
4. Carbon is insoluble in all known solvents.

10.2 FUELS

A fuel is a substance which burns in air with the liberation of much heat energy.

(a) Gaseous fuels

1. Producer gas; 2. Water gas; 3. Coal gas; 4. Natural gas.

(b) Liquid fuels

1. Petrol } Petroleum products
2. Oil }

(c) Solid fuels

1. Wood; 2. Peat; 3. Lignite; 4. Coal; 5. Coke; 6. Anthracite; 7. Smokeless fuels.

The value of a fuel is assessed by its *calorific value*, this being the heat obtained by combustion of a definite amount of fuel (usually expressed in calories per gram or British Thermal Units per pound, or cubic foot).

1 calorie is the heat required to raise 1 gram of water 1 degree centigrade

1 Btu is the heat required to raise 1 lb of water 1 degree fahrenheit

Calorific values can also be quoted in *joules*, e.g. ordinary coal 7,500 cal/g, petrol 10,000 cal/g.

Calorific values are used in nutrition studies, e.g. butter 7·9 kilocal/g, sugar 4·1 kilocal/g, potatoes 0·7 kilocal/g.

Water gas and producer gas

When air is passed over red-hot coke, producer gas is formed.

$$2C + \overbrace{O_2 + 4N_2}^{\text{air}} \rightarrow 2CO + 4N_2 \quad \Delta H = -27 \text{ kilocalories (evolved)}$$

When steam is passed over white-hot coke, water gas is formed.

$$C + H_2O \rightarrow CO + H_2 \quad \Delta H = +32 \text{ kilocalories (absorbed)}$$

The hot coke in a large cylindrical container has air and steam passed through it alternately. The air raises the temperature and the steam lowers it. If the air and steam are passed in in the correct quantities to maintain the temperature constant, semi-water gas (Mond gas) is formed.

Water gas is a better fuel than producer gas (the nitrogen here will not burn).

A mixture of carbon monoxide and hydrogen, similar to water gas, is formed from methane (ex petroleum oil), as mentioned in 6.3.

Uses of water gas (or any mixture of carbon monoxide/hydrogen) include:

1. Fuel
2. Manufacture of hydrogen (see 6.3)
3. Manufacture of methanol CH_3OH*

$$CO + 2H_2 \xrightarrow{ZnO,\ Cr_2O_3,\ 400°C,\ 300\ atm} CH_3OH$$

---

* Methanol is a component of "methylated spirit."

By altering the conditions, higher alcohols are formed. Producer gas is used mainly as a fuel.

The production of town gas

Within a few years, it seems likely that only about 50 per cent of town gas will be derived from coal. Basically, modern gas can be regarded as having three main components, (*a*) the lean gas (mainly hydrogen), (*b*) the enriching gas (e.g. methane), (*c*) the inert ballast (e.g. nitrogen and carbon dioxide) to keep a constant density. The enriching gas is needed since the town gas is sold at a declared calorific value which is often greater than that of the basic gas.

The price of coal suitable for gas-making has risen sharply over the past few years (over 80 per cent rise, 1954–64), whereas the price of oil has risen far less sharply. Improvements to the standard gas-works procedure (to be discussed shortly) have followed the following lines:

(*a*) Production of lean gas from cheaper forms of coal.
(*b*) Production of lean gas from petroleum fractions.
(*c*) Use of natural gas.
(*d*) Use of fuel gas (mainly methane) from other sources.

The standard gas works procedure

Coal gas is a mixture of gases formed by destructive distillation of coal and contains, by volume, about 50 per cent hydrogen, together with methane, carbon monoxide, ethylene, and small amounts of other gases.

The distillate from coal also contains many other valuable chemicals which are undesirable in the gas to be used domestically, but which are needed in other ways. The equipment of the gas works is therefore concerned primarily with the removal of such materials. The layout of a typical plant is shown in fig. 10.2.

The coal is distilled in vertical retorts, the residue (coke) being withdrawn at the bottom and the coal put in at the top. The retorts are heated by burning producer gas; the coke not required for producer gas manufacture is cooled and used as a fuel. From the retort, the brown/yellow volatile material passes through long lengths of tubing to cool it (these tubes may be air- or water-cooled); much tar and ammonia solution condense out of the volatile material (the water comes from the coal) and are run out of the bottom of the condenser. The gases then pass through a rotary pump (exhauster) which drives the gas through the remaining stages. In the Livesey washer, the gas is forced upwards through perforated metal plates immersed in water; here more ammonia is absorbed and tar (which is present in the gas as a

The Gas Works

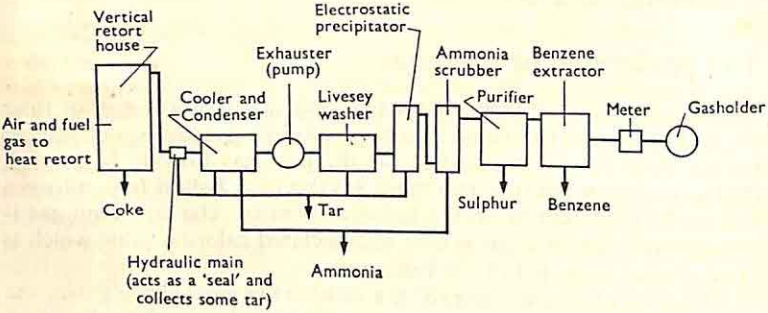


FIG. 10.2

fog) is removed. The electrostatic precipitator removes the rest of the tar; the gas passes upwards through a chamber containing two metal plates between which a large potential difference is maintained, the tar particles becoming electrically charged and sticking to the plates. Final removal of ammonia is accomplished in the scrubber where the gas, travelling upwards, meets a downward stream of water passing over rotating paddles. The purifier removes hydrogen sulphide. It consists of trays of moist hydrated ferric oxide, and the removal of hydrogen sulphide can be represented as follows:

$$2Fe(OH)_3 + 3H_2S \rightarrow Fe_2S_3 + 6H_2O$$

The oxide must be kept wet and slightly alkaline for the reaction to occur. The 'spent oxide' is exposed to air when sulphur is liberated and the oxide regenerated.

The gas is then treated to remove benzene by washing the gas with oil (from which the benzene can be removed by fractional distillation) or by passing the gas over activated charcoal which adsorbs (takes on to its surface) the benzene (from which it can be subsequently be distilled off). Charcoal (but not oil) also removes carbon disulphide from the gas. If this is not done, the carbon disulphide can be removed by passing the gas over nickel at 450°C.

$$CS_2 + \underset{\text{(in gas)}}{2H_2} \rightarrow 2H_2S + C$$

The hydrogen sulphide is then removed as previously mentioned. The gas is finally passed through a meter and stored in a gasholder.

Gasification of low grade coal

This principle is used in the Lurgi process, which originated in Germany in 1927, the first full scale plant operating in 1936. After many tests it was found that British low grade coals were suitable for the process and a plant was opened by the Scottish Gas Board at Westfield in 1961. The gas-making vessel is similar to that in a producer gas or water gas plant. Lurgi gas is generated by the reaction of steam and oxygen with the coal at about 30 atmospheres pressure. Some form of stirring is needed to prevent 'caking' of the coal. Proportions of steam and oxygen are controlled so that the reaction is exothermic. No coke is formed, but some tar and other by-products are recovered. Enrichment of the gas is necessary.

Gasification of oil

Several factors have led to the introduction of oil gasification on a large scale, e.g. relative price movement of oil compared with coal, easier handling of oil because of its fluid state, and the ready availability of petroleum fractions.

There are many types of plant used in the United Kingdom and these fall into the following main categories:

(*a*) *Cyclic steam reforming*, e.g. the Onia-Gegi process.
This can be represented:

$$C_mH_n + mH_2O \rightleftharpoons nCO + (m + \tfrac{1}{2}n)H_2$$

and

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

The reaction vessel contains a nickel catalyst and is heated by a mixture of air and vaporized oil 'feedstock'. When a temperature of about 900°C is reached, air is replaced by steam. Waste heat in the first part is used to produce steam and vaporize the feedstock, where this is insufficiently volatile.

The process can produce either a gas which can be used direct, or one which can easily be enriched to town gas requirements. The calorific value of the gas depends on the feedstock and exact operating temperature.

(*b*) *Continuous catalytic reforming*

Here the vaporized feedstock, mixed with steam, is passed under pressure through a number of alloy tubes packed with a catalyst (containing nickel). The reaction taking place is endothermic and heat is provided by burning light oil distillate around each tube. The gas is purified by removal of carbon monoxide (see later) and enriched to town gas requirements. It is claimed that the raw materials can be converted to processed gas in as little as 90 seconds.

(c) *Enriched gas from oil*

Gas is often 'lean' when first produced and so requires enriching to the required calorific value. One way in which this can be done is to add methane or butane.

Use of natural gas

Natural gas consists mainly of methane. Use is now being made of the natural gas deposits in the Sahara. Searches have been made for natural gas in the North Sea (and gas was discovered there in Dec. 1965) and another major source has been found in Holland. Much methane is used for enriching and for reforming to town gas.

Detoxification of town gas

For some time carbon monoxide has been removed from town gas in order to lessen the chance of accidental poisoning. This is usually done by applying the 'water gas shift reaction'.

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

The gas is mixed with steam and passed over a catalyst of chromic and ferric oxides at 400°C, converting all but 2 or 3 per cent of carbon monoxide to the dioxide. This can be absorbed and hydrogen sulphide removed in several ways, including washing with diethanolamine, absorption in activated potassium carbonate solution, or absorption in hot potassium carbonate solution.

$$CO_3^{--} + CO_2 + H_2O \rightarrow 2HCO_3^-$$
$$CO_3^{--} + H_2S \rightarrow HCO_3^- + HS^-$$

Coal tar

Coal tar is a black viscous liquid which is fractionally distilled to give a variety of products:

Table 10.2

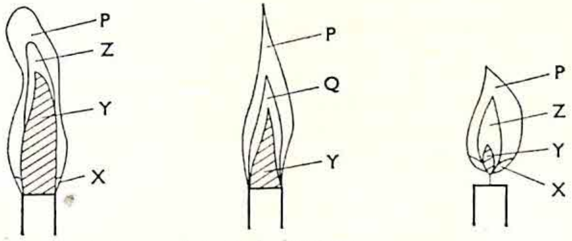
Tar

	Light oil (b.p. up to 170°C)	*Middle oil* (*Carbolic oil*) (b.p. 170–230°C)	*Heavy oil* (*Creosote oil*) (b.p. 230–270°C)	*Green oil* (*anthracene oil*) (b.p. 270–360°C)	*Residue* (*pitch*)
	↓ benzene toluene xylenes	↓ phenols cresols		↓ naphthalene anthracene	
% by vol.	2	8	16	12	62

Benzene is used as a solvent, in motor spirit, and in the manufacture of many compounds, e.g. nylon. Toluene is used in the manufacture of explosives (e.g. T.N.T.). Naphthalene is used in making dyestuffs and mothballs. Phenol is used in making plastics, dyestuffs, and as an antiseptic. Pitch is used for roofing buildings.

Ammoniacal liquor contains about 2 per cent ammonia. It is converted to ammonium sulphate for use as a fertilizer.

Flames are formed when gases react together to give so much heat that the products become incandescent (give out light). A substance will not burn until its temperature exceeds the *ignition temperature*.



(a) **Types of flame produced with the bunsen burner** (b) **Candle flame**

Luminous Non-luminous

(i) Air holes shut (ii) Air holes open

Fig. 10.3

X = blue zone, complete combustion
Y = cold zone, unburnt gas
Z = yellow zone, incomplete combustion
P = mauve zone, non-luminous, complete combustion
Q = light blue zone, incomplete combustion

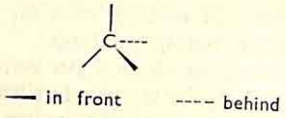
Table 10.3

	Luminous	*Non-luminous*
1.	Unsteady	Steady
2.	Not very hot	Hotter
3.	Quiet	Noisy
4.	Deposits soot on plate held in it	Deposits no soot
5.	Pure gas burns in air	Gas/air mixed and burned in air

10.3 TERMS USED IN ORGANIC CHEMISTRY

Organic chemistry is the chemistry of carbon compounds. It is extensive because carbon atoms can link in chains and rings.

The valency of carbon in all stable compounds is four, the covalent bonds being directed towards the corners of a tetrahedron.



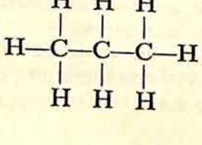
An *homologous series* is a series of compounds in which every member can be prepared by similar methods, has similar chemical properties, can be represented by a general formula, and each member differs from the preceding one by the addition of a methylene $=CH_2$ group, for example:

Paraffins C_nH_{2n+2}
Primary aliphatic alcohols $C_nH_{2n+1}.OH$

A *functional group* is an atom or group of atoms which determines the characteristic reactions of a particular homologous series. Thus, all alcohols contain the hydroxyl group ($-OH$), all primary amines contain the amino group ($-NH_2$), etc.

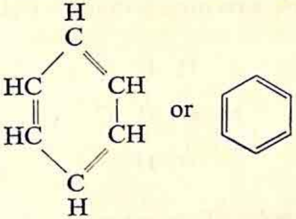
Groups of general formula C_nH_{2n+1} are called alkyl groups, e.g. methyl CH_3, ethyl C_2H_5, propyl C_3H_7.

Organic compounds can be classified as *aliphatic* or *aromatic*. The former contain open chains of carbon atoms, e.g.

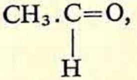
propane


$$\begin{array}{ccccccc} & & H & & H & & H & \\ & & | & & | & & | & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & \\ & & H & & H & & H & \end{array}$$

while the latter contain one or more benzene rings



If a compound contains atoms linked by single covalent bonds, it is said to be *saturated*, e.g. propane $CH_3.CH_2.CH_3$, ethanol $CH_3.CH_2.OH$.

If a compound contains atoms linked by double or triple covalent bonds, it is said to be *unsaturated*, e.g. ethylene $H_2C{=}CH_2$, acetylene $HC{\equiv}CH$, acetaldehyde  $CH_3.\underset{\displaystyle H}{\underset{|}{C}}{=}O$, methyl cyanide $CH_3.C{\equiv}N$.

The *empirical formula* of a compound is the simplest possible formula, giving the relative number of each kind of atom in the molecule. It can be determined from an analysis of the pure compound.

Example: The empirical formula of benzene is CH.

The *molecular formula* is the formula representing the actual number of each kind of atom in the molecule. It is deduced from the empirical formula and the molecular weight.

Example: The molecular weight of benzene is 78, i.e. its molecular formula is $(CH)_6$ or C_6H_6, since the weight of the empirical unit is 13.

The *structural formula* of a compound is the formula giving the manner in which the atoms are arranged within the molecule.

Example: Benzene has a ring structure (see earlier in this section).

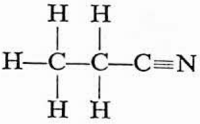
The structural formula can be deduced only after an extensive examination of the properties of the compound.

Example on calculation of empirical formula

A compound had C 65·45 per cent, H 9·09 per cent, N 25·45 per cent. Its M.Wt was 55.

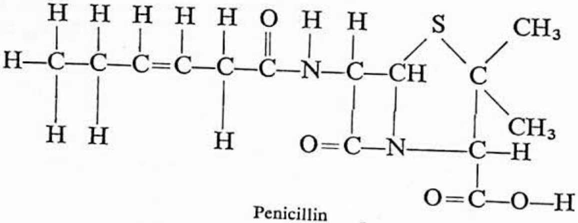
	C	: H	: N
% composition	65·45	9·09	25·45
Relative number of atoms present *% composition* divided by *At. wt.*	$\frac{65·45}{12}$ 5.45	$\frac{9·09}{1}$ 9·09	$\frac{25·45}{14}$ 1·82
Divide by smallest	3	5	1

empirical formula = C_3H_5N (wt = 55 units), i.e. molecular formula is also C_3H_5N. A possible structural formula is C_2H_5CN (ethyl cyanide).

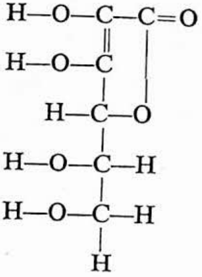


$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}C{\equiv}N}$$

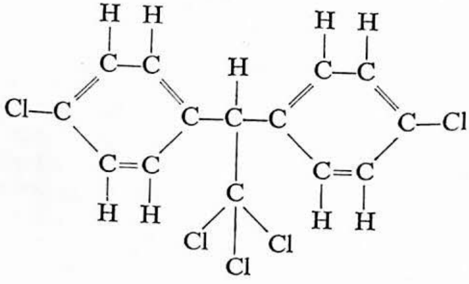
The structural formulae of some compounds are very complicated, for example:



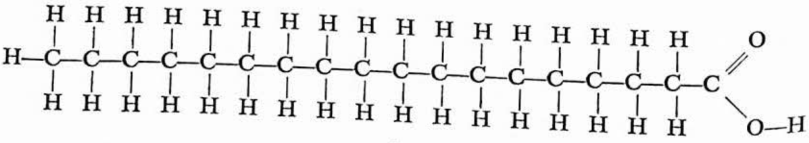
Penicillin



Vitamin C



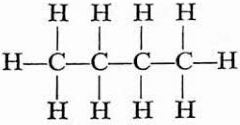
D.D.T. (an insecticide)



Stearic Acid

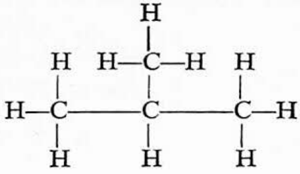
Isomerism is said to occur when two or more compounds have the same molecular formula but different physical or chemical properties. These compounds have different structural formulae, for example:

n-butane

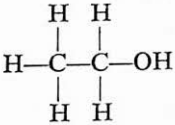


$$\begin{array}{ccccccccc} & & H & & H & & H & & H & \\ & & | & & | & & | & & | & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & \\ & & H & & H & & H & & H & \end{array}$$

iso-butane

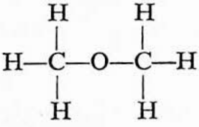


ethanol



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & OH \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

dimethyl ether

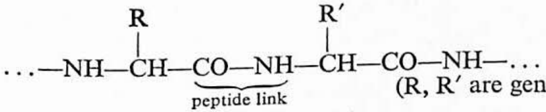


$$\begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & - & C & - & O & - & C & - & H \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array}$$

Polymerization is the name given to the process whereby two or more simple molecules (monomers) are joined together to form a new compound (polymer) of the same empirical formula but higher molecular weight. This refers to addition polymerization. In condensation polymerization, small molecules such as water, are eliminated. In copolymerization, two or more different monomers are present.

Natural polymers include proteins (e.g. fibroin in silk, keratin in hair) and starch (a condensation polymer of glucose molecules).

Proteins have the general formula



$$\ldots\text{—NH—}\overset{\displaystyle R}{\overset{|}{\text{CH}}}\text{—}\underbrace{\text{CO—NH}}_{\text{peptide link}}\text{—}\overset{\displaystyle R'}{\overset{|}{\text{CH}}}\text{—CO—NH—}\ldots$$

(R, R′ are generally alkyl groups)

On warming with a dilute mineral acid, a protein is hydrolysed (7.11) to a mixture of amino acids, having a general formula

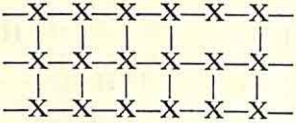
$$R.CH(NH_2).COOH,$$

e.g. glycine $NH_2.CH_2.COOH$. This mixture of acids can be separated by chromatography (1.6).

Plastics are man-made polymers. A *plastic* is a substance of high molecular weight which, at some stage during its manufacture, can be moulded by heat or pressure (or both). Thermosoftening plastics become soft when heated and can be softened and moulded several times without change of properties. They have structures with linear chains of carbon atoms.

$$\text{—X—X—X—X—X—X—}$$

Thermosetting plastics are infusible once set and cannot be remoulded. Their structures consist of a network of carbon atoms.



Plastics can have their properties altered by plasticizers and can be coloured by dyes and pigments. Fillers are used to increase the bulk of the plastic.

Examples

Thermosoftening: polythene (polyethylene) $(C_2H_4)_n$, polyvinyl chloride (P.V.C.) $(H_2C-CHCl)_n$, polystyrene $(C_6H_5.CH-CH_2)_n$.

Polythene can be manufactured by heating ethylene at 200°C under a pressure of 1000 atm or at a lower pressure in the presence of certain catalysts. It is an excellent electrical insulator, is easily moulded, blown, or cast into films, and is readily coloured. It is used for packaging and coating materials, making household goods such as beakers, making pipes, and for insulation (e.g. transatlantic telephone cable).

P.V.C. is resistant to fire and weathering and is a good electrical insulator. It is used for making household goods, for electrical insulation, for leathercloth, for drainpipes and gutters, and for toys.

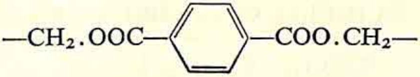
Thermosetting plastics include bakelite (phenol/formaldehyde resin), and urea or melamine/formaldehyde resins. Both urea/formaldehyde and melamine/formaldehyde can be coloured easily and can be moulded under pressure to form tableware (e.g. Melaware). They can be used as ion-exchange resins, e.g. to deionize water, as the NH_2 groups present combine with acidic groups in the water.

Synthetic fibres include nylon 66 and terylene. The former contains peptide links

$$-(CH_2)_6.NH.CO.(CH_2)_4.CO.NH-$$

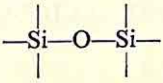
Nylon 66 can easily be prepared on a small scale as follows: 5 drops of dilute ammonia solution are added to 5 cm³ of 5 per cent aqueous hexamethylenediamine. Then 5 cm³ of 5 per cent adipyl chloride solution (in carbon tetrachloride) are cautiously added, ensuring that the layers do not mix. A thread of nylon can be drawn from the interface with a fine wire loop.

Terylene is a condensation polymer of ethylene glycol $(CH_2OH)_2$ and terephthalic acid $HOOC.C_6H_4.COOH$, the structure being



It forms permanent creases (in trousers, skirts, etc).

Silicones are polymers containing siloxy-chains.



$$-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Si}}}-$$

They have several valuable properties, e.g. water-repellency, electrical insulation, anti-stick, anti-foam, constancy of physical properties over a wide range of temperature, etc.

10.4 METHANE CH_4 (marsh gas, firedamp)

Methane is a paraffin hydrocarbon (alkane), compounds of the general formula C_nH_{2n+2}.

It can be prepared by heating anhydrous sodium acetate CH_3COONa with soda lime (effectively sodium hydroxide).

$$CH_3COO^- + OH^- \rightarrow CH_4\uparrow + CO_3^{--}$$

This is a general method for paraffins, e.g. ethane C_2H_6 can be made by heating anhydrous sodium propionate C_2H_5COONa with soda lime.

Methane alone can be made by treating aluminium carbide with water.

$$\underset{(4Al^{+++},\ 3C^{----})}{Al_4C_3} + 12H_2O \rightarrow 4Al^{+++}(OH^-)_3\downarrow + 3CH_4\uparrow$$

Methane is a colourless gas which is insoluble in water (molecules of hydrocarbons do not interact with water molecules).

It burns in air forming carbon dioxide and steam.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \Delta H = -213 \text{ kilocalories (evolved)}$$

Because methane is a *saturated compound* it reacts by *substitution*, for example:

1. With chlorine in diffused sunlight.

$$CH_4 + Cl_2 \rightarrow \underset{\text{methyl chloride (monochloromethane)}}{CH_3Cl} + HCl$$

$$CH_3Cl + Cl_2 \rightarrow \underset{\text{methylene dichloride (dichloromethane)}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \rightarrow \underset{\text{chloroform (trichloromethane)}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \rightarrow \underset{\text{carbon tetrachloride (tetrachloromethane)}}{CCl_4} + HCl$$

2. With nitric acid in the vapour state at 500°C, nitromethane is formed.

$$CH_4 + HNO_3 \rightarrow CH_3NO_2 + H_2O$$

Uses

1. Fuel.
2. Making hydrogen (6.3) and methanol (see uses of water-gas).
3. Making carbon black and acetylene.

$$CH_4 \xrightarrow{1200^\circ C} C + 2H_2$$

$$2CH_4 \xrightarrow{1500^\circ C} C_2H_2 + 3H_2$$

N.B. Ethane C_2H_6 is present in natural gas and has properties similar to those of methane.

Carbon black is compounded into rubber to strengthen tyres, and is also used in printer's ink.

10.5 CRUDE OIL

This has been formed in oil wells by the decomposition of animals and plants by bacteria under very high pressure. Oil, together with 'natural gas', is found in shallow parts of seas where the water contains an abundance of animal and vegetable life, and plenty of micro-organisms.

Crude oil can be separated by fractional distillation into the following fractions:

Table 10.4

OIL

Gas	*Petrol*	*Kerosene*	*Light gas oil*	*Heavy gas oil*	*Residue*
(b.p. below 40°C)	(b.p. 40–175°C)	(b.p. 150–240°C)	(b.p. 220–250°C)	(b.p. 250–350°C)	(b.p. above 350°C)

The residue is separated by further fractional distillation under reduced pressure into lubricating oils, greases, waxes and bitumen (used to make roads, as an insulation material, etc).

The paraffin gases and vapours can be separated by gas chromatography (see 1.6).

The petrol fraction contains a mixture of low molecular weight hydrocarbons with straight-chain structures. These are liable to cause 'knocking' (premature combustion in the cylinder of the engine) and are converted to 'branched' or ring compounds, which cause much less knocking, by various processes including reforming (heating under pressure to give ring compounds), catalytic reforming (the same as reforming except that a catalyst is used, e.g. platinum), polymerization, and alkylation (formation of 'branched' chain compounds). A petrol can be improved by the addition of 'antiknock', lead tetra-ethyl, $Pb(C_2H_5)_4$, but the detailed mechanism is not known.

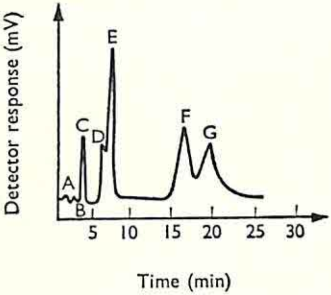


FIG. 10.4

Separation of petroleum fraction, adsorbed on alumina, by hydrogen.

A = air B = ethane
C = propane D = isobutane
E = butane F, G = pentanes

The light gas oil can be broken down into hydrocarbons with lower molecular weight by 'cracking' (thermal or catalytic). The process gives mainly olefins plus a range of liquids. In a 'cat-cracker', the vapour is passed over a catalyst of silica and alumina at 400–500°C. The liquid distillate from cracking contains many valuable 'branched' hydrocarbons (used as petrols).

The heavy oil is used as diesel oil.

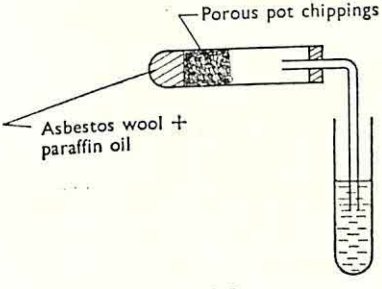


FIG. 10.5

Paraffin oil can be 'cracked' on a small scale by pouring it into a test-tube to a depth of about 1 inch, adding asbestos wool to soak up the liquid, filling about 3 inches of the tube with porous pot chippings, and heating the middle of the tube. If the gases are passed into bromine water (or dilute alkaline potassium permanganate), the reagent is decolourized, showing that an olefin is present.

10.6 ETHYLENE C_2H_4

Ethylene (ethene) is an olefin hydrocarbon (alkene), compounds of general formula C_2H_{2n}. It can be prepared by heating ethanol with excess concentrated sulphuric acid at 160°C.

$$C_2H_5OH - H_2O \rightarrow C_2H_4\uparrow$$

Commercially, it is obtained by the 'cracking' of a fraction from petroleum oil. A mixture of olefins is obtained which can be fractionated. To obtain a high yield of lower members of the olefin series, rather than higher members, the petroleum fraction is cracked with steam at 700°C.

It can also be made by the 'cracking' of ethane at high temperatures.

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

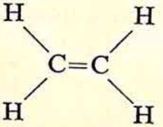
Ethylene is a gas which is insoluble in water.

It burns in air forming carbon dioxide and water.

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \quad \Delta H = -334 \text{ kilocalories (evolved)}$$

It is an *unsaturated* compound which contains a double covalent bond.

$H_2C{=}CH_2$ or



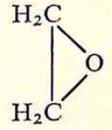
It therefore reacts primarily by *addition*, for example:

1. With bromine in carbon tetrachloride it gives ethylene dibromide. The bromine is decolourized, and this serves as a test for the unsaturation of ethylene. Bromine water is also decolourized.

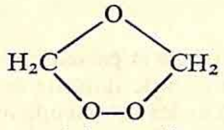
$$H_2C{=}CH_2 + Br_2 \rightarrow \underset{\text{ethylene dibromide}}{BrH_2C{-}CH_2Br}$$

2. It has similar reactions with hydrogen bromide (to give ethyl bromide CH_3CH_2Br), hydrogen in the presence of nickel at 150°C (to give ethane $CH_3{-}CH_3$), concentrated sulphuric acid at room temperature (to give ethyl hydrogen sulphate $CH_3CH_2HSO_4$), dilute alkaline potassium permanganate (to give ethylene glycol $HOCH_2{-}CH_2OH$, this

being the addition of hydroxyl groups, OH, and since the permanganate is decolourized again serving as a test for the unsaturation of ethylene), oxygen in the presence of a silver catalyst (to give ethylene oxide, see below), and ozone (to give ethylene ozonide, see below).



ethylene oxide



ethylene ozonide

Ethylene polymerizes to give polythene (polyethylene), $(C_2H_4)_n$. The conditions used are high pressures and 200°C in the presence of oxygen as catalyst.

10.7 ACETYLENE C_2H_2

Acetylene (ethyne) is an acetylene hydrocarbon (alkyne), compounds of general formula C_nH_{2n-2}.

It is prepared by dropping water on calcium carbide, acetylene being evolved as a colourless gas, and collected over water. This can be thought of as the displacement of the weak acid C_2H_2 by the stronger one H_2O.

$$Ca^{++}(C{\equiv}C)^{--} + 2H_2O \rightarrow C_2H_2\uparrow + Ca^{++}(OH^-)_2$$

It burns in air forming carbon dioxide and water.

$$C_2H_2 + \tfrac{5}{2}O_2 \rightarrow 2CO_2 + H_2O \quad \Delta H = -313 \text{ kilocalories (evolved)}$$

It is an *unsaturated* compound with a triple covalent bond.

$$H{-}C{\equiv}C{-}H$$

It therefore reacts primarily by addition, e.g.:

1. With chlorine in the presence of iron filings and silica (to moderate the reaction) it gives 1:2 dichloroethylene and 1:1, 2:2 tetrachloroethane.

$$HC{\equiv}CH + Cl_2 \rightarrow \underset{\text{1:2 dichloroethylene}}{ClHC{=}CHCl}$$

$$ClHC{=}CHCl + Cl_2 \rightarrow \underset{\text{1:1, 2:2 tetrachloroethane}}{Cl_2HC{-}CHCl_2}$$

2. With hydrogen in the presence of nickel at 150°C it gives ethylene, then ethane.

$$HC{\equiv}CH + H_2 \rightarrow H_2C{=}CH_2 : H_2C{=}CH_2 + H_2 \rightarrow H_3C{-}CH_3$$

3. With hydrogen chloride, vinyl chloride and ethylidene dichloride are formed.

$$HC{\equiv}CH + HCl \rightarrow \underset{\text{vinyl chloride}}{H_2C{=}CHCl} : H_2C{=}CHCl + HCl \rightarrow \underset{\text{ethylidene dichloride}}{CH_3{-}CHCl_2}$$

4. When acetylene is passed into dilute sulphuric acid at 60°C in the presence of mercuric sulphate as catalyst, acetaldehyde (CH_3CHO) is formed. Aldehydes are compounds of the general formula $R.CHO$, where R is an alkyl group (in the aliphatic series). The reaction is effectively the addition of the elements of water.

$$HC{\equiv}CH + H_2O \rightarrow CH_3CHO$$

Acetylene polymerizes when passed through a red-hot glass tube to give some benzene.

$$3HC{\equiv}CH \xrightarrow{\text{heat}} \underset{\text{benzene}}{C_6H_6}$$

Acetylene forms red cuprous acetylide when passed into ammoniacal cuprous chloride solution. The ammonia removes any hydrochloric acid which would be formed (this would decompose the acetylide).

$$C_2H_2 + 2CuCl + 2NH_3 \rightarrow \underset{\text{red}}{Cu_2C_2\downarrow} + 2NH_4Cl$$

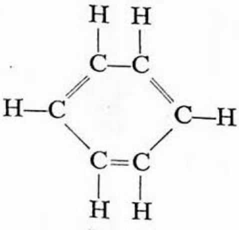
With ammoniacal silver nitrate solution, yellow silver acetylide Ag_2C_2 is formed.

These reactions enable acetylene to be distinguished from ethylene.

10.8 BENZENE C_6H_6

Benzene is the simplest aromatic hydrocarbon. It is obtained either from coal tar (by fractional distillation) or from petroleum oil.

It has the structure shown below.



Benzene

Benzene ought, from its formula, to react in a manner similar to that of ethylene, but it is much less reactive. This means that its structure cannot really be represented as simply as given above, but the latter will suffice for the present study.

Benzene is a colourless liquid (b.p. 80°C) which is insoluble in water, though soluble in organic solvents.

It burns with a smoky flame to give carbon dioxide and water.

$$C_6H_6 + \tfrac{15}{2}O_2 \rightarrow 6CO_2 + 3H_2O \quad \Delta H = -783 \text{ kilocalories (evolved)}$$

It reacts primarily by substitution, for example:

1. With chlorine in the presence of a 'halogen carrier', such as iron filings or iodine, it gives chlorobenzene.

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$$

2. With a mixture of concentrated nitric and sulphuric acids, not exceeding 50°C, it gives nitrobenzene.

$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$$

3. With hot concentrated sulphuric acid, it gives benzene sulphonic acid.

$$C_6H_6 + H_2SO_4 \rightleftharpoons C_6H_5SO_2O^-H^+ + H_2O$$

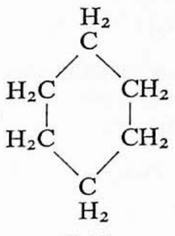
4. With methyl chloride in the presence of anhydrous aluminium chloride, it gives toluene (the Friedel-Crafts reaction).

$$C_6H_6 + CH_3Cl \rightarrow C_6H_5CH_3 + HCl$$

Benzene also undergoes addition reactions, from example:

1. With hydrogen in the presence of nickel at 150°C, cyclohexane is formed.

$C_6H_6 + 3H_2 \rightarrow$



C_6H_{12}

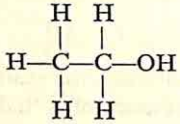
2. With ethylene in the presence of anhydrous aluminium chloride, ethyl benzene is formed

$$C_6H_6 + C_2H_4 \rightarrow C_6H_5.C_2H_5$$

10.9 ETHANOL (ETHYL ALCOHOL) C_2H_5OH

Ethanol is a primary aliphatic alcohol, these being compounds of the general formula R—CH_2OH, where R is an alkyl group. All primary alcohols contain the grouping —CH_2OH.

Ethanol has the structure shown below.



$$\begin{array}{ccccc} & & H & & H & \\ & & | & & | & \\ H & — & C & — & C & —OH \\ & & | & & | & \\ & & H & & H & \end{array}$$

It is formed when sucrose or glucose is fermented by yeast, for example:

$$\underset{\text{glucose}}{C_6H_{12}O_6} \rightarrow 2C_2H_5OH + 2CO_2\uparrow$$

It can be manufactured by the above method, or by heating ethyl hydrogen sulphate (obtained from ethylene) with water.

$$C_2H_5HSO_4 + H_2O \rightarrow C_2H_5OH + H_2SO_4$$

It is a colourless liquid which is soluble in water (owing to the formation of hydrogen bonds with the water molecules, see 2.16).

It burns in air to give carbon dioxide and water.

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O \quad \Delta H = -327 \text{ kilocalories (evolved)}$$

It reacts with sodium to form sodium ethylate, and hydrogen is evolved.

$$2C_2H_5OH + 2Na \rightarrow \overbrace{2C_2H_5O^- + 2Na^+} + H_2\uparrow$$

When *dry*, it reacts with phosphorus pentachloride to give ethyl chloride and hydrogen chloride (the evolution of this indicates that an hydroxyl group is present).

$$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + \underset{\substack{\text{phosphorus}\\ \text{oxychloride}}}{POCl_3} + HCl\uparrow$$

It can be oxidized by acidified potassium dichromate or potassium permanganate to form acetaldehyde (CH_3CHO) and then acetic acid (CH_3COOH).

It reacts with acetic acid in the presence of hydrogen ions as catalyst to give ethyl acetate—an ester, a compound of general formula RCOOR′, where R and R′ are alkyl groups, e.g. CH_3, C_2H_5, or acyl groups, e.g. C_6H_5 (phenyl).

$$CH_3COOH + C_2H_5OH \rightleftharpoons \underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

The general esterification reaction is

$$\text{ACID} + \text{ALCOHOL} \rightleftharpoons \text{ESTER} + \text{WATER}$$

With concentrated sulphuric acid (excess) at 160°C it gives ethylene (10.6) (removal of 1 mol. of water from 1 mol. of ethanol).

If the temperature is 140°C and excess alcohol is used, diethyl ether is formed (removal of 1 mol. of water from 2 mol. of ethanol).

$$2C_2H_5OH - H_2O \rightarrow C_2H_5OC_2H_5$$

Ethanol reacts with concentrated sulphuric acid at room temperature to give ethyl hydrogen sulphate (an esterification, using an inorganic acid).

$$C_2H_5OH + H_2SO_4 \rightarrow C_2H_5HSO_4 + H_2O$$

Ethanol reacts with chlorine in the presence of an alkali to give chloroform $CHCl_3$, and with iodine in the presence of an alkali to give iodoform CHI_3 (a yellow precipitate), this distinguishing it from the poisonous methanol CH_3OH. The chloroform reaction involves (i) oxidation, (ii) chlorination, (iii) hydrolysis.

$$\underset{\text{ethanol}}{C_2H_5OH} \xrightarrow{\text{oxidation}} \underset{\text{acetaldehyde}}{CH_3.CHO} \xrightarrow{\text{chlorination}} \underset{\text{chloral}}{CCl_3.CHO}$$

$$\xrightarrow{\text{hydrolysis}} \underset{\text{chloroform + formic acid}}{CHCl_3 + HCOOH}$$

$$\begin{array}{c} \downarrow \text{ neutralized} \\ HCOONa \end{array}$$

10.10 ETHYLAMINE $C_2H_5NH_2$

Ethylamine is a primary amine, these being compounds of the general formula R—NH_2, where R is an alkyl group in the aliphatic series. All primary amines contain the grouping —NH_2.

Ethylamine is formed when ethyl iodide (or chloride, or bromide, but the iodide is preferred since it has the highest boiling point) is treated with concentrated ammonia solution.

$$C_2H_5I + 2NH_3 \rightarrow C_2H_5NH_2 + NH_4^+ + I^-$$

It is a colourless gas which has a fishy odour. It dissolves in water (with the attendant formation of hydrogen bonds, cf. ammonia) to give an alkaline solution (cf. ammonia solution).

$$C_2H_5NH_2 + H_2O \rightarrow \underset{\text{ethylammonium hydroxide}}{C_2H_5NH_3^+ + OH^-}$$

It is therefore a base since it accepts a proton.
It reacts with acids to give salts, for example:

$$C_2H_5NH_2 + HCl \rightarrow \underset{\substack{\text{ethylammonium chloride}\\ \text{(cf. ammonium chloride } NH_4{}^+Cl^-\text{)}}}{\overbrace{C_2H_5NH_3^+ + Cl^-}}$$

It reacts with nitrous acid to give ethanol, nitrogen and water.

$$C_2H_5NH_2 + HNO_2 \rightarrow C_2H_5OH + N_2\uparrow + H_2O$$

In general

$$R{-}NH_2 + HNO_2 \rightarrow R{-}OH + N_2\uparrow + H_2O$$

that is

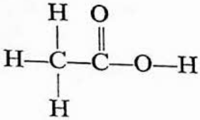
$$\underset{\text{amine}}{R{-}NH_2} \rightarrow \underset{\text{alcohol}}{R{-}OH}$$

It reacts with chloroform and alcoholic potassium hydroxide to give the evil-smelling gas ethyl isocyanide, C_2H_5NC.

It reacts with a solution containing cupric ions to form a deep blue solution containing a complex ion (cf. reaction of ammonia solution with cupric ions).

10.11 ACETIC ACID CH_3COOH

Structure



$$H{-}\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}H$$

Acetic acid can be prepared by oxidation of ethanol with *excess* acidified sodium dichromate solution.

$$C_2H_5OH + [O] \rightarrow \underset{\text{acetaldehyde}}{CH_3CHO} + H_2O$$

$$CH_3CHO + [O] \rightarrow \underset{\text{acetic acid}}{CH_3COOH}$$

It used to be manufactured by the oxidation of ethanol by air in the presence of certain bacteria (Mycoderma Aceti). Vinegar is a dilute solution of acetic acid and is obtained by fermenting wine in such a way as to convert the ethanol present into acetic acid.

Acetic acid is now manufactured mainly by the oxidation of acetaldehyde (which can be obtained from the coal or oil industry) by air in the presence of a cobalt acetate catalyst.

$$2CH_3CHO + O_2 \rightarrow 2CH_3COOH$$

Acetic acid is a colourless liquid which is readily soluble in water. It has a highly pungent odour (of vinegar).

It is a weak acid (see 3.1).

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

It reacts with bases to form salts and with alcohols to form esters, for example:

$$CH_3COOH + Na^+ + OH^- \rightarrow \underset{\text{sodium acetate}}{CH_3COO^- + Na^+} + H_2O$$

$$CH_3COOH + C_2H_5OH \rightleftharpoons \underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

Acetic acid reacts with phosphorus pentachloride to form acetyl chloride, the hydroxyl group of the acid being replaced by a chlorine atom.

$$CH_3COOH + PCl_5 \rightarrow \underset{\text{acetyl chloride}}{CH_3COCl} + \underset{\substack{\text{phosphorus}\\ \text{oxychloride}}}{POCl_3} + HCl\uparrow$$

If chlorine is bubbled into glacial acetic acid in the presence of a catalyst (e.g. red phosphorus), a mixture of chloroacetic acids is formed. This is an example of *substitution.*

$$\left.\begin{array}{rl} CH_3COOH + Cl_2 \rightarrow HCl + ClH_2C.COOH & \text{mono-} \\ \downarrow\quad & \\ Cl_2HC.COOH & \text{di-} \\ \downarrow\quad & \\ Cl_3C.COOH & \text{tri-} \end{array}\right\} \begin{array}{l}\text{chloroacetic}\\ \text{acids}\end{array}$$

10.12 FOODSTUFFS

A complete diet consists of six classes of substance:

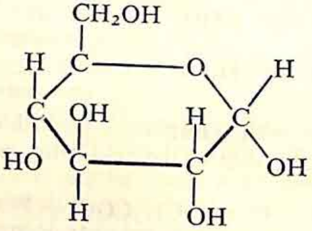
(*a*) Carbohydrates	(*b*) Fats	(*c*) Proteins
(*d*) Mineral salts	(*e*) Vitamins	(*f*) Water

Carbohydrates and fats can be regarded as 'fuels', providing energy for muscular activity and keeping us warm. Proteins and mineral salts are body-building foods, entering into the structure of hair, nails, teeth, etc. Vitamins and water are needed for healthy functioning of the body.

Carbohydrates

Carbohydrates are compounds of carbon, hydrogen and oxygen (although the term is now used to cover compounds containing nitrogen and sulphur as well), the last two named elements being present in the proportion in which they exist in water. A carbohydrate can therefore be formulated as $C_x(H_2O)_y$. In a normal diet the main carbohydrates are sugars (e.g. in sugar itself, sweet foods such as honey, ripe fruits, etc) and starches (e.g. in potatoes, rice, sago, flour, wheat, rye).

Many compounds can be classified as *sugars*. Glucose (dextrose, grape sugar) is an example of a simple sugar called a *monosaccharide*. Its molecular formula is $C_6H_{12}O_6$ and the structure is as follows:



Sugars such as sucrose (cane or beet sugar), maltose (malt sugar) and lactose (milk sugar) have the formula $C_{12}H_{22}O_{11}$ (*disaccharides*) and their structures consist of two monosaccharide units linked together with the elimination of a water molecule.

Table sugar is sucrose. It occurs in plants, where it is formed during photosynthesis, and the main sources of supply are cane sugar and sugar beet. The beet or cane is crushed and the sugar extracted with hot water. The solution is decolourized (e.g. with animal charcoal) and then concentrated until crystals form on cooling.

Disaccharides can be converted to monosaccharides by (*a*) warming with a dilute acid, (*b*) by use of an enzyme; when eaten, the enzyme ptyalin in the saliva can bring about decomposition.

Starch is a *polysaccharide*, in which many glucose units are linked together with the elimination of a water molecule between each pair of units, forming a large long chain molecule. The formula can be written $(C_6H_{10}O_5)_n$. Starch can be broken down to glucose by heating with almost any dilute acid. This is used in the manufacture of glucose. When starch is eaten, enzymes in saliva carry out the degradation.

Starch is also degraded to glucose by enzymes in malt and yeast and this takes place in brewing; other enzymes are present in yeast to decompose glucose to ethanol and carbon dioxide.

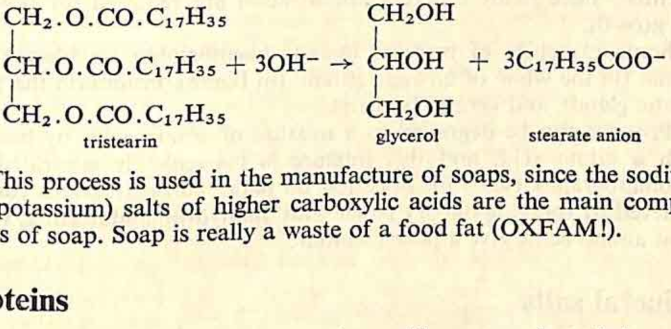
$$\text{Starch} \xrightarrow[\text{malt and yeast}]{\text{Enzymes in}} \text{Glucose} \xrightarrow[\text{yeast}]{\text{Enzymes in}} \underset{C_2H_5OH}{\text{Ethanol}} + CO_2\uparrow$$

Pure starch is a white solid which is only sparingly soluble in cold water, but which forms a colloidal 'starch solution' in hot water. This liquid sets on cooling to starch paste. Starch is used as a stiffening agent in laundry work, in the manufacture of paper, and as a 'filler' in many products.

Fats

Fats and oils act as reserve food supplies; they are stored in the body and used as required. Animal fats are present in foodstuffs such as butter, eggs and lard, while plant fats are present in olive oil, soya beans, peanuts, etc. Many naturally occurring oils cannot be eaten, but can be hydrogenated to solid edible fats (see 6.5); margarine is made in this way.

Fats are esters formed between the higher alcohol glycerol (like ethanol) and higher carboxylic acids (acids similar to acetic acid); they are known as tri-glycerides. Mutton fat contains tristearin, a compound of glycerol and stearic acid ($C_{17}H_{35}COOH$). When this fat is heated with sodium hydroxide solution, *saponification* occurs to give glycerol and the sodium salt of stearic acid.



$$\begin{array}{l} CH_2.O.CO.C_{17}H_{35} \\ | \\ CH.O.CO.C_{17}H_{35} \\ | \\ CH_2.O.CO.C_{17}H_{35} \\ \text{tristearin} \end{array} + 3OH^- \rightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{glycerol} \end{array} + \underset{\text{stearate anion}}{3C_{17}H_{35}COO^-}$$

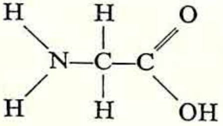
This process is used in the manufacture of soaps, since the sodium (or potassium) salts of higher carboxylic acids are the main components of soap. Soap is really a waste of a food fat (OXFAM!).

Proteins

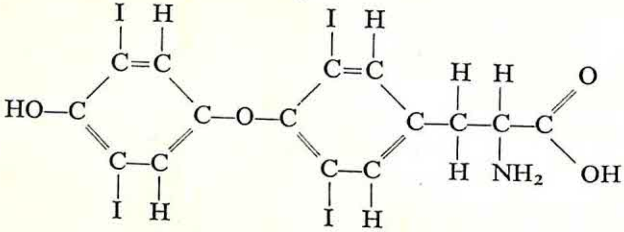
These can supply energy by reaction with oxygen but their main function is to maintain growth and repair of animal or plant cells. Foods having a high proportion of animal protein include meat, fish, eggs, milk and cheese. Foods containing much vegetable protein include cereals, nuts, fruit and many vegetables.

Proteins are complex substances, their molecules being composed of many amino acid units joined together. Two typical amino acids are glycine and thyroxine.

Glycine (amino-acetic acid)



Thyroxine



In a typical protein, about twenty amino acids link together to give a polymer with a molecular weight of about 15,000 to several millions. Proteins are broken down by digestive juices in the stomach and intestine forming their constituent amino acids and these then recombine to form compounds needed for cell growth. A mixed diet is essential, since many different amino acids are required for healthy cell growth.

Some examples of proteins include haemoglobin (in blood), albumin (in the white of an egg), gelatin (in bones), insulin (in the pancreatic gland), and keratin (in hair).

Proteins can be degraded to a mixture of amino acids by heating with a dilute acid, and this mixture is conveniently separated by chromatography (see 1.6). Location on paper chromatograms can be achieved by spraying the dry paper with 'ninhydrin' and heating, when most amino acids give a purple colour.

Mineral salts

Although the body contains elements such as carbon, hydrogen, oxygen and nitrogen, many others are vital for health. *Sulphur* is a component of many proteins, *Iodine* is needed for correct functioning of the thyroid gland (deficiency causes goitre and mental and physical debility); although iodine is provided by fish, green vegetables and dairy produce, in areas where foods such as the two latter varieties are likely to be deficient in iodine, and where fish is scarce, it is convenient to use iodized table salt. *Iron* is a constituent element in haemoglobin and deficiency causes anaemia; it can be obtained by eating liver, oatmeal, eggs, potatoes and green vegetables. *Fluorine* is required for healthy teeth; in many areas it is added to drinking water and many toothpastes contain it in the form of a fluoride (e.g. stannic fluoride). *Calcium*, *phosphorus* and *magnesium* occur in milk, cheese and green vegetables and are required for healthy teeth, bones and nerve tissues. Other necessary elements include *copper*, *silicon*, *potassium*. *Sodium chloride* is taken into the body in the form of table salt. It occurs in body fluids (including blood) and is excreted in perspiration.

Vitamins

The word vitamin was first used by Funk (1912), but the idea of such substances as 'accessory food factors' had been suggested rather earlier by Hopkins. Deficiency in vitamins causes what are known as 'deficiency diseases'. Some vitamins have been synthesized and can be taken in the form of pills by those who need them.

Hormones

These are compounds which play an important part in bodily processes although they are not present in foods. They are secreted by various glands in the body and their secretion causes stimulation of definite parts of the body. Thus, certain glands regulate definite bodily processes. Adrenalin (from the suprarenal gland, near the kidney) can cause nervousness if secreted in too large a quantity. Hormones secreted by the thyroid gland (in the throat, just below the Adam's apple) and the pituitary gland (at the base of the brain) control growth. Excessive action of the pituitary gland causes excessive growth. Arrested development of the thyroid gland can cause cretinism (gross deformity and idiocy). The pancreas secretes digestive juices plus insulin, a deficiency of the latter causing diabetes. Various hormones are secreted by the sex glands.

Plants can have their growth affected by hormones, e.g. selective weed killers often contain hormones injurious to the growth of weeds, though not to other plants. Hormone rooting powders for striking cuttings are very common.

Table 10.5

Vitamins

Vitamin and date of isolation	*Chemical name, formula and date of synthesis*	*Main source of supply*	*Effect of deficiency*
A 1937	Related to carotene $C_{20}H_{30}O$ 1945	Fish liver oils, milk, butter, egg yolk, carrots	Poor growth Night blindness Xerophthalmia
B_1 1931	Aneurin or Thiamin $C_{12}H_{18}ON_4SCl_2$ 1936	Wholemeal or brown bread. Yeast extract, e.g. Marmite. Wheat germ, e.g. Bemax. Egg yolk, nuts, oatmeal, liver, kidney	General debility Beri-beri
B_2 1933	Riboflavin $C_{17}H_{20}N_4O_6$ 1935	Yeast, lean meat, liver, eggs, cheese, green vegetables	General debility
C 1925	Ascorbic acid $C_6H_8O_6$ 1933	Fresh fruits and vegetables	Poor resistance to disease Scurvy Haemorrhage
D 1930	Calciferol $C_{28}H_{44}O$	Fish liver oils, milk, butter, cheese, eggs. (Formed in body in sunlight)	Poor bone and teeth formation. Rickets
E 1936	α-Tocopherol $C_{29}H_{50}O_2$ 1938	Green vegetables, meat, eggs	Loss of fertility and muscular decay

Many other vitamins, e.g. B_3, B_4, B_5, B_6, P and K, are also of great importance.

Cellulose

Cellulose is a polysaccharide which can be broken down into glucose (cf. starch). It cannot, however, be broken down in the body and therefore can never be digested by humans; it can be digested by cows, horses, sheep, and other animals which eat grass. Cellulose provides valuable 'roughage' in the human body.

Cellulose and similar compounds occur in the cell walls of all plants, e.g. in fibrous materials such as wood, cotton, hemp, grass, straw, wool.

Cellulose is used in the manufacture of textiles, paper, string, rayon, plastics (e.g. cellulose acetate, celluloid, cellophane), explosives (e.g. gun-cotton), and lacquers.

Tests for foodstuffs

(*a*) *Starch*. A dilute solution of iodine gives a deep blue colour. Green leaves are first killed by dipping in boiling water, bleached by dipping in alcohol, warmed on a water bath, softened by wetting with water, and finally tested with dilute iodine solution.

(*b*) *Sugars* (reducing). Fehling's solution A is added to the solution to be tested, then Fehling's B until a clear deep blue solution is formed. If this is boiled, a rust-coloured precipitate of cuprous oxide Cu_2O is formed, owing to reduction of cupric ions in the Fehling's A by the sugar.

(*c*) *Fats*. If a fat is rubbed on a thin piece of paper, a permanent clear spot is produced.

Alternatively, if a fat is shaken with Sudan IV, the droplets of fat will be stained red.

(*d*) *Proteins*. If Millon's reagent is added and the solution boiled, a brick red precipitate indicates the presence of a protein.

10.13 THERMAL DECOMPOSITION (PYROLYSIS) OF ORGANIC COMPOUNDS

Many organic compounds can be decomposed by heat, some examples being as follows:

(*a*) Methane gives carbon black and hydrogen at about 1200°C

$$CH_4 \rightarrow C + 2H_2$$

At about 1500°C it gives acetylene.

$$2CH_4 \rightarrow C_2H_2 + 3H_2$$

(*b*) Paraffins can often be 'cracked' (see 10.5) to give olefins, for example:

$$\underset{\text{ethane}}{C_2H_6} \rightarrow \underset{\text{ethylene}}{C_2H_4} + H_2$$

$$\underset{\text{propane}}{C_3H_8} \rightarrow \underset{\text{ethylene}}{C_2H_4} + \underset{\text{methane}}{CH_4}$$

(*c*) Acetaldehyde decomposes on strong heating to give methane and carbon monoxide (the mechanism of this is very complicated and of the 'chain' type).

$$CH_3CHO \rightarrow CH_4 + CO$$

(*d*) Acetone decomposes on strong heating to give methane and ketene.

$$CH_3COCH_3 \rightarrow CH_4 + \underset{\text{ketene}}{H_2C{=}C{=}O}$$

(*e*) Sugars decompose on heating to give carbon and water, e.g. sucrose.

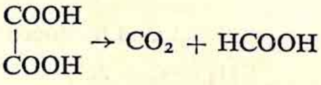
$$C_{12}H_{22}O_{11} \rightarrow 12C + 11H_2O$$

(*f*) Wood (containing the compounds cellulose (see 10.12) and lignin (a polymer containing aromatic rings to which are attached methoxyl groups, OCH_3)), decomposes on heating in the absence of air forming carbon plus a volatile material. The latter can be condensed to pyroligneus acid, which can be further separated into methanol CH_3OH, acetic acid CH_3COOH, and a little acetone CH_3COCH_3, as well as other substances.

(*g*) Thermal decomposition of acetic acid is best achieved by heating the sodium salt of the acid with 'soda lime' (see 10.4). The molecule effectively loses carbon dioxide and is said to have been *decarboxylated.*

$$CH_3COO^-Na^+ + Na^+ + OH^- \rightarrow 2Na^+ + CO_3^{--} + \underset{\text{methane}}{CH_4\uparrow}$$

(*h*) Oxalic acid decomposes on heating forming formic acid.



$$\begin{array}{c}COOH\\ |\\ COOH\end{array} \rightarrow CO_2 + HCOOH$$

(*i*) Calcium acetate decomposes on heating to give acetone.

$$(CH_3COO^-)_2Ca^{++} \rightarrow Ca^{++}CO_3^{--} + CH_3COCH_3$$

A similar reaction is the decomposition of acetic acid when passed over a hot metallic oxide (such as manganous oxide, MnO).

$$2CH_3COOH \rightarrow CH_3COCH_3 + H_2O + CO_2$$

10.14 OXIDES OF CARBON

Carbon dioxide CO_2

Preparation

(*a*) Reaction of a dilute mineral acid with a metallic carbonate—dilute hydrochloric acid is normally reacted with calcium carbonate in a Kipp's apparatus. The principle is that carbonic acid (weak acid) is displaced by the stronger acid and then the carbonic acid, being unstable, decomposes into carbon dioxide and water.

$$CO_3^{--} + 2H^+ \rightarrow CO_2\uparrow + H_2O$$

(*b*) A by-product of brewing.

$$\text{Sugar} + \underset{\substack{\text{(contains}\\\text{enzymes)}}}{\text{Yeast}} \rightarrow \text{Ethanol} + CO_2\uparrow \quad \text{(see 10.9)}$$

(*c*) Action of heat on carbonates of metals below sodium in the electrochemical series, e.g. $MgCO_3$ can be decomposed fairly readily at 300–500°C.

Industrially, carbon dioxide can be made by heating calcium carbonate in a 'lime kiln'.

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

(*d*) By burning any carbonaceous material in excess air or oxygen.

$$C + O_2 \rightarrow CO_2$$

Properties

It is a colourless, odourless gas, heavier than air (soap bubble blown with the gas sinks in air), soluble in water under pressure (e.g. in soda and mineral waters), and is easily liquefied and solidified by cooling (the solid is called 'dry ice'; this sublimes on allowing it to warm up to room temperature).

Carbon dioxide is an acidic oxide. It is slightly soluble in water at normal pressures (1 cm^3 per cm^3) giving an acidic solution, assumed to contain carbonic acid.

$$H_2O + CO_2 \rightleftharpoons H_2CO_3$$

Carbonic acid decomposes on heating.

It forms two series of salts, the carbonates (containing CO_3^{--} ions) and bicarbonates (containing HCO_3^- ions), for example:

$$2OH^- + CO_2 \rightarrow CO_3^{--} + H_2O$$
$$CO_3^{--} + H_2O + CO_2 \rightarrow 2HCO_3^-$$

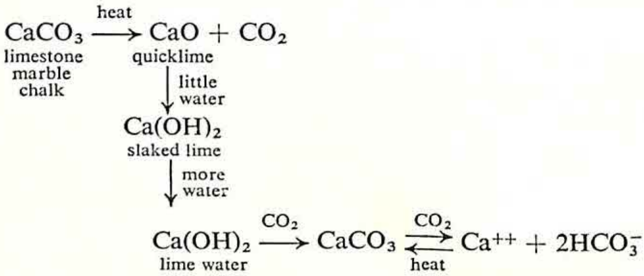
Carbon dioxide turns limewater milky owing to the formation of calcium carbonate.

$$Ca^{++} + 2OH^- + CO_2 \rightarrow CaCO_3\downarrow + H_2O$$

If carbon dioxide is passed in for some time (i.e. *excess* carbon dioxide), soluble calcium bicarbonate is formed and the suspension goes to a clear solution (see 'hardness of water', 7.11).

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca^{++} + 2HCO_3^-$$

These reactions are part of a large cycle involving carbon dioxide:



The percentage of carbon dioxide in the air remains at about 0·03 per cent since the input balances the output.

Table 10.6

Input	*Output*
1. Burning of carbon compounds	1. Photosynthesis (see 7.2)
2. Respiration of animals and plants	2. Dissolved in rain water
3. Fermentation	
4. Decay of animal and vegetable matter	
5. Hot springs and volcanoes	

Carbon dioxide is used in mineral waters (dissolved under pressure, as a preservative), as dry ice (ice cream transit, acetone/dry ice freezing mixtures, etc), in fire extinguishers (these rely on the fact that (*a*) it is heavier than air and therefore 'blankets' the fire, (*b*) it does not burn or support combustion unless the substance burning has a *very* hot flame), and also as a coolant in atomic reactors.

Very strongly burning substances (e.g. magnesium) can continue to burn in carbon dioxide, decomposing it.

$$2Mg + CO_2 \rightarrow \underset{\text{white}}{2MgO} + \underset{\text{black}}{C}$$

Carbon cycle

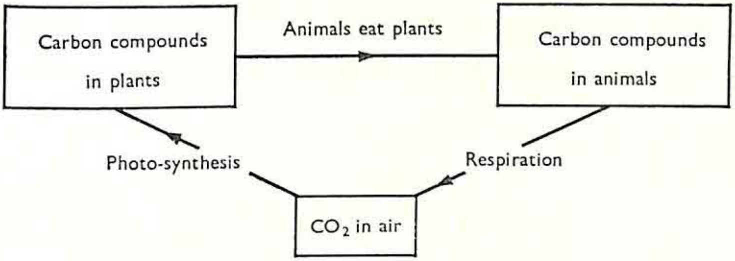


FIG. 10.6

Test for carbonates and bicarbonates

(*a*) Carbonates *give off* (evolve) carbon dioxide with hydrochloric acid in the cold.

(*b*) Carbonates of metals other than Na, K (and NH_4) give off carbon dioxide when heated.

(*c*) Bicarbonates of sodium and potassium can be recognized as follows:

1. The solids and their solutions give off carbon dioxide when heated. The residues give off carbon dioxide when reacted with hydrochloric acid.
2. The solutions are neutral to phenolphthalein but alkaline to litmus and methyl orange.

   N.B. Solutions of the carbonates of these metals are alkaline to the usual indicators.
3. With magnesium sulphate solution, they give no white precipitate whereas solutions of the carbonates would give a white precipitate of magnesium carbonate.

$$Mg^{++} + 2HCO_3^- \rightarrow \underset{\text{soluble}}{Mg(HCO_3)_2}$$

$$Mg^{++} + CO_3^{--} \rightarrow MgCO_3\downarrow$$

Carbon monoxide CO

Preparation (not advisable to do so in quantity)

(*a*) Reduction of carbon dioxide when passed through red-hot carbon.

$$CO_2 + C \rightarrow 2CO$$

Reduction of CO_2 to CO

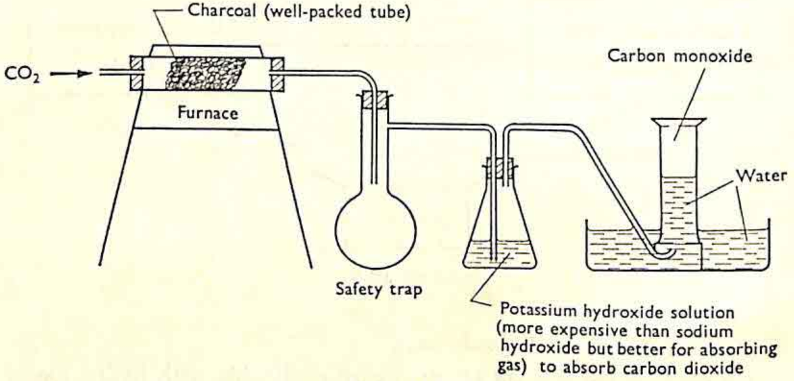

Charcoal (well-packed tube)
CO_2
Furnace
Carbon monoxide
Water
Safety trap
Potassium hydroxide solution (more expensive than sodium hydroxide but better for absorbing gas) to absorb carbon dioxide

FIG. 10.7

This type of reaction occurs in the blast furnace and in the domestic coal fire.

(*b*) Burning of carbon in a restricted supply of air.

$$2C + O_2 \rightarrow 2CO$$

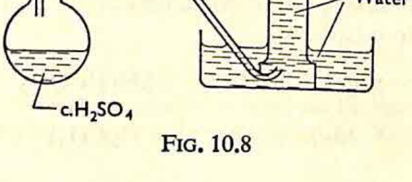
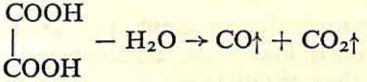


FIG. 10.8

(*c*) Dehydration of formic acid (or formates) with concentrated sulphuric acid (8.8)—this requires no heat as the reaction is exothermic.

$$H.COOH - H_2O \rightarrow CO\uparrow$$

(*d*) Dehydration of oxalic acid (and oxalates) by concentrated sulphuric acid—this requires heat.



$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} - H_2O \rightarrow CO\uparrow + CO_2\uparrow$$

Method (*d*) gives carbon dioxide as well and this can be removed by absorption in potassium hydroxide solution.

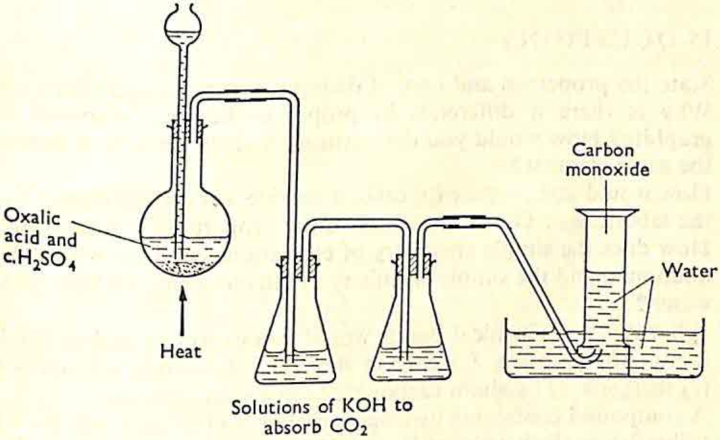

Carbon monoxide
Oxalic acid and c.H_2SO_4
Water
Heat
Solutions of KOH to absorb CO_2

FIG. 10.9

(*e*) Carbon monoxide is a constituent of many gaseous fuels, e.g. coal gas, water gas, producer gas.

Properties

It is a colourless gas with no smell. It is VERY poisonous, since it combines chemically and irreversibly with haemoglobin in the blood to form carboxyhaemoglobin, preventing oxygen from being carried around the body as oxyhaemoglobin.

The carboxy-compound is cherry red in colour. Carbon monoxide has about the same density as air, is practically insoluble in water, although it is absorbed by ammoniacal cuprous chloride forming the substance $CuCl.CO.2H_2O$, cf. acetylene gives a red precipitate with this reagent (see 10.7).

It burns with a blue flame, forming carbon dioxide (the test for it); the formation of carbon dioxide distinguishes carbon monoxide from hydrogen.

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \quad \Delta H = -68 \text{ kilocalories (evolved)}$$

It is an important reducing agent. For example, it reduces hot oxides of metals fairly low in the electrochemical series, some salts (e.g. ammoniacal silver nitrate to silver at room temperature), etc, for example:

$$Fe_2O_3 + 3CO \rightleftharpoons 2Fe + 3CO_2$$
$$PbO + CO \rightarrow Pb + CO_2$$

10.15 QUESTIONS

1. State the properties and uses of diamond, graphite and charcoals.

2. Why is there a difference in properties between diamond and graphite? How would you demonstrate that they are both forms of the same element?

3. How would you prepare (*a*) carbon dioxide, (*b*) carbon monoxide in the laboratory? Give an account of the properties of these oxides.

4. How does the simple chemistry of ethylamine compare with that of ammonia, and the simple chemistry of ethanol compare with that of water?

5. What types of chemical bonds would you expect to find in (*a*) diamond, (*b*) graphite, (*c*) carbon dioxide, (*d*) carbon tetrachloride, (*e*) methane, (*f*) sodium carbonate? Give your reasons.

6. A compound containing hydrogen, carbon and oxygen only gave the following analysis results: $H = 4{\cdot}35\%$, $C = 26{\cdot}09\%$, $O = 69{\cdot}56\%$. Find the empirical formula of the compound. [$(CH_2O_2)_x$]

7. Find the empirical formula of a substance having the following percentage composition: $Na = 18{\cdot}55\%$, $S = 25{\cdot}8\%$, $O = 19{\cdot}35\%$, water of crystallization $= 36{\cdot}3\%$. [$Na_2S_2O_3.5H_2O$]

8. Find the empirical formula of starch, which has the composition:

$$C = 44{\cdot}4\%,\ H = 6{\cdot}2\%,\ O = 49{\cdot}4\% \text{ (by weight). } [(C_6H_{10}O_5)_x]$$

9. A compound of nitrogen and hydrogen contains $87{\cdot}5\%$ nitrogen by weight. Find the simplest formula [$(NH_2)_x$]

11 Phosphorus and its Compounds

11.1 OCCURRENCE AND MANUFACTURE OF PHOSPHORUS

Phosphorus does not occur in the free state. It is found as metallic phosphates, e.g. calcium phosphate $Ca_3(PO_4)_2$ in the ore Rock phosphate (in the U.S.A.). Calcium phosphate is also present in bones.

Phosphorus exhibits allotropy, existing as white and violet allotropes in the solid state. White phosphorus is made first and then converted to the violet form if required.

Rock phosphate is reduced with hot carbon in an electrothermal furnace at about 1500°C, silica being added (as granite chips) to form a slag of calcium silicate. The silica *displaces* the more volatile phosphoric oxide from calcium phosphate.

Manufacture of phosphorus

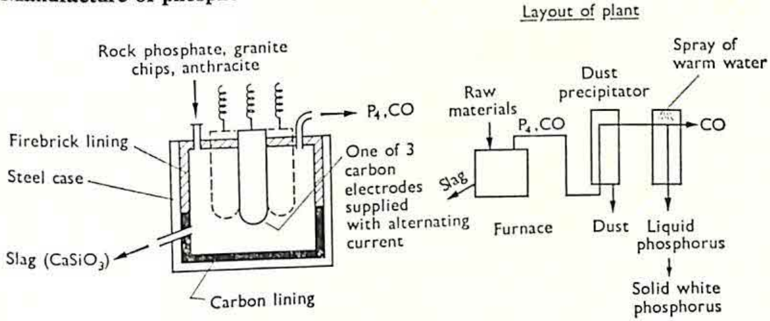


FIG. 11.1

$$Ca_3(PO_4)_2 \equiv \underset{\text{basic}}{3CaO} + \underset{\text{acidic}}{P_2O_5}$$

$$3CaO + 3SiO_2 \rightarrow \underset{\text{calcium silicate slag}}{3CaSiO_3}$$

$$2P_2O_5 + 10C \rightarrow P_4\uparrow + 10CO\uparrow$$

[Compare the reactions:

$$\text{(i) } CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2CO_3 \nearrow H_2O + CO_2\uparrow$$

$$\text{(ii) } Ca_3(PO_4)_2 + 3SiO_2 \rightarrow 3CaSiO_3 + P_2O_5]$$

The phosphorus vapour and carbon monoxide leave the furnace, are purified by electrostatic dust precipitation, and the phosphorus is then condensed to a liquid. This is pumped away through heated pipes and cast into sticks of the white allotrope. This must be kept out of contact with air (kept under water).

Violet phosphorus can be made by heating white phosphorus very strongly in the absence of air. The more common 'red' phosphorus (not a separate allotrope, but an intimate mixture of violet and a little white phosphorus) is made by heating white phosphorus at about 250°C in a steel pot with only a small opening to the air (this prevents atmospheric oxidation). The change is catalysed by substances such as iodine, but they are not used industrially. Any white phosphorus not converted to the red form is removed by reaction with sodium hydroxide solution.

Red or violet phosphorus can be converted to the white form by condensing the vapour formed by heating red phosphorus (white is the metastable allotrope and has more energy than violet; hence, there is less energy change in passing from the vapour to white phosphorus than in passing to violet phosphorus).

Table 11.1

Comparison of the allotropes

White	*Violet*
1. Less stable; passes very slowly to violet form	More stable
2. White waxy solid, structure based on P_4 units (tetrahedral shape)	Violet, brittle solid, structure based on P_4 units joined together
3. Specific gravity 1.8	Specific gravity (red) 2.2
4. Soluble in CS_2	Insoluble in CS_2
5. Very poisonous	Not very poisonous
6. Glows in dark owing to oxidation to P_2O_5 (chain mechanism)	Does not glow
7. Ignites in air at about 35°C forming P_2O_5	Violet phosphorus does not ignite in air unless the temperature is very high; red phosphorus ignites at about 250°C forming P_2O_5
8. Reacts with hot conc. NaOH solution forming phosphine and sodium hypophosphite	No reaction with alkalis

$$4P + 3OH^- + 3H_2O \rightarrow 3H_2PO_2^- + PH_3\uparrow$$

White phosphorus is MORE REACTIVE than the violet form.

Evidence that white and violet (red) phosphorus are one and the same element

1. Either form can be changed into the other by altering the physical conditions without addition or removal of any other substance.
2. Equal weights of the two forms, when heated in a stream of oxygen, give equal weights of phosphorus pentoxide.

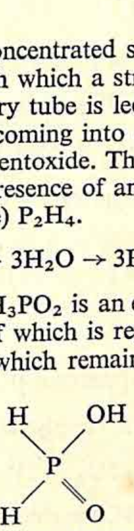
11.2 PHOSPHINE PH_3

Preparation

White phosphorus and a concentrated solution of sodium hydroxide are boiled in a flask through which a stream of coal gas is passed to exclude all air. If the delivery tube is led into a trough of water, the gaseous product ignites on coming into contact with the air, forming white rings of phosphorus pentoxide. The phosphine is spontaneously inflammable owing to the presence of an impurity called liquid phosphorus hydride (diphosphine) P_2H_4.

$$4P + 3OH^- + 3H_2O \rightarrow 3H_2PO_2^- + PH_3\uparrow$$

Hypophosphorous acid H_3PO_2 is an example of an acid with three hydrogen atoms only one of which is replaceable; hence the formula of sodium hypophosphite, which remains in solution in the flask, is NaH_2PO_2.



(basicity determined by the number o
–OH groups)

Properties

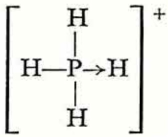
Phosphine is a colourless, poisonous gas with a fish-like smell. It is only very slightly soluble in water and the solution is feebly alkaline.

$$PH_3 + H_2O \rightarrow PH_3.H_2O \quad \text{(or } PH_4OH\text{)}$$

It is much less basic than the related compound ammonia NH_3 (nitrogen and phosphorus are in the same family (Group VB) of the Periodic Table).

Its most stable salt is phosphonium iodide $PH_4^+I^-$.

The phosphonium ion has a structure similar to that of the ammonium ion.



$$\left[\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H}-\mathrm{P}\rightarrow\mathrm{H} \\ | \\ \mathrm{H} \end{array}\right]^{+}$$

11.3 OXIDES OF PHOSPHORUS

Phosphorus sesquioxide, phosphorous oxide, phosphorus trioxide P_2O_3

Phosphorus is burnt in a limited supply of air.

$$4P + 3O_2 \rightarrow 2P_2O_3$$

It is a white waxy solid which gives phosphorous acid with cold water.

$$P_2O_3 + 3H_2O \rightarrow 2H_3PO_3$$

Its formula should be written P_4O_6 according to the known structure of the compound, which is based on the tetrahedral distribution of atoms in the P_4 unit.

Phosphoric oxide, phosphorus pentoxide P_2O_5

Phosphorus is burnt in a liberal supply of air.

$$4P + 5O_2 \rightarrow 2P_2O_5$$

It is a white crystalline solid, very deliquescent, and a good drying agent. With cold water it gives metaphosphoric acid HPO_3 (exothermic reaction), a transparent, glassy solid.

$$P_2O_5 + H_2O \rightarrow 2HPO_3$$

With excess cold water, or with hot water, it gives orthophosphoric acid H_3PO_4 (a colourless crystalline solid).

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$$

When orthophosphoric acid is heated at 215°C, pyrophosphoric acid (a white solid) is formed.

$$2H_3PO_4 \rightarrow H_4P_2O_7 + H_2O$$

The formula of phosphorus pentoxide should be written P_4O_{10} in order to represent accurately the known crystal structure of the compound.

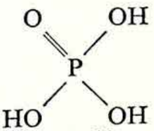
11.4 ORTHOPHOSPHORIC ACID H_3PO_4

This is made by oxidation of red phosphorus with concentrated nitric acid.

$$\begin{array}{l} 20HNO_3 + 10e \rightarrow 10NO_3^- + 10H_2O + 10NO_2 \\ 2P + 8H_2O - 10e \rightarrow 2PO_4^{---} + 16H^+ \\ \hline 20HNO_3 + 2P \rightarrow 10NO_3^- + 2H_2O + 10NO_2 + 2PO_4^{---} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad + 16H^+ \\ \therefore\ \ \underline{10HNO_3 + P \rightarrow 5NO_3^- + H_2O + 5NO_2\uparrow + PO_4^{---} + 8H^+} \end{array}$$

and $3H^+ + PO_4^{---} \rightleftharpoons H_3PO_4$

It is a syrupy liquid which can, with difficulty, be crystallized. It is a tribasic acid and forms three sodium salts:



(basicity determined by number of —OH groups)

$$\left.\begin{array}{l}\text{sodium dihydrogen orthophosphate } Na^+H_2PO_4^- \\ \text{disodium hydrogen orthophosphate } (Na^+)_2HPO_4^{--}\end{array}\right\}\begin{array}{l}\text{ACID SALTS}\\ \text{(see 6.7, 6.8)}\end{array}$$

$$\left.\begin{array}{l}\text{trisodium orthophosphate } (Na^+)_3PO_4^{---}\end{array}\right\}\begin{array}{l}\text{NORMAL SALT}\\ \text{(see 6.7, 6.8)}\end{array}$$

By a longstanding convention, ordinary laboratory 'sodium phosphate' is the disodium salt.

When dissolved in water, the monosodium salt gives a solution which is acidic to litmus, the disodium salt a solution which is just alkaline to litmus while the trisodium salt gives a solution strongly alkaline to litmus. [Note that NaH_2PO_4 solution is about neutral to methyl orange, but acidic to phenolphthalein; Na_2HPO_4 solution is slightly alkaline to phenolphthalein, and strongly alkaline to methyl orange.] In each case the salt is hydrolysed (see 7.11) to sodium hydroxide and orthophosphoric acid, the former being a strong alkali (3.1) and the latter a weak acid (3.1). In the mono- and disodium salts, however, the effect of the sodium hydroxide is partially counteracted by the hydrogen ions they provide in solution owing to the fact that they are acid salts.

Calcium orthophosphate $Ca_3(PO_4)_2$

This occurs naturally in rock phosphate. It is used in the manufacture of phosphorus (11.1) and superphosphate (8.8). The latter is soluble in water, whereas calcium phosphate is not very soluble, and so acts much more rapidly when used as a fertilizer.

Test for phosphate ions in solution

Add a solution of ammonium molybdate, and a little concentrated nitric acid, boil and allow to stand. A canary yellow precipitate is obtained if a phosphate is present. If the test is carried out in the cold, precipitation is slow.

11.5 CHLORIDES OF PHOSPHORUS

Phosphorus trichloride PCl_3

Pass dry chlorine over white phosphorus melted in an atmosphere of coal gas or carbon dioxide. The phosphorus trichloride is distilled and condenses as a colourless liquid which fumes in moist air owing to hydrolysis. It is a typical covalent compound (2.9).

Preparation of phosphorus trichloride

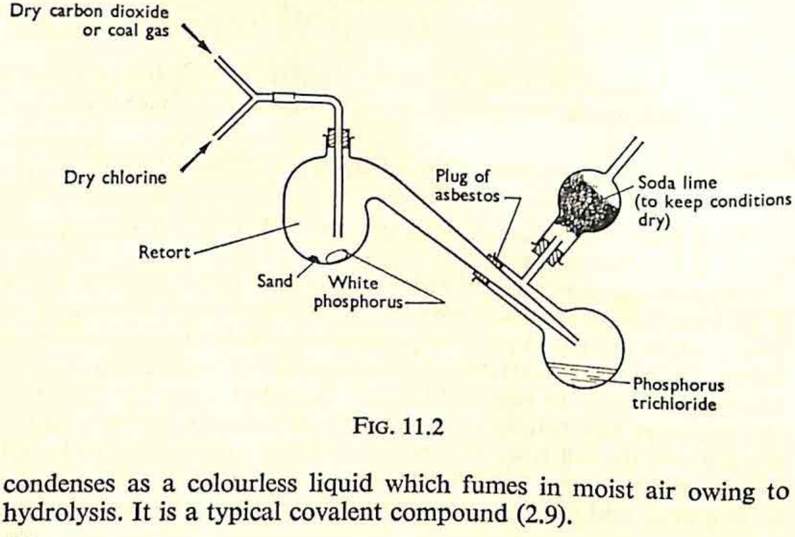


FIG. 11.2

$$2P + 3Cl_2 \rightarrow 2PCl_3$$

$$PCl_3 + 3H_2O \rightarrow \underset{\text{phosphorous acid}}{H_3PO_3} + 3HCl\uparrow$$

Phosphorus pentachloride PCl_5

Pass dry chlorine into phosphorus trichloride until it is all changed into the pentachloride (a white solid).

$$PCl_3 + Cl_2 \rightleftharpoons PCl_5$$

It is hydrolysed by water in two stages:

$$PCl_5 + H_2O \rightarrow \underset{\text{phosphorus oxychloride}}{POCl_3} + 2HCl\uparrow$$

$$POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl\uparrow$$

On heating, it undergoes thermal dissociation (1.5) and the percentage of dissociation at a given temperature can be deduced from vapour density (2.22) measurements.

11.6 USES OF PHOSPHORUS AND ITS COMPOUNDS

1. White phosphorus is used in rat poison. It was once used in heads of matches, but this is now illegal.
2. *Matches:* Ordinary match heads contain phosphorus trisulphide P_4S_3, potassium chlorate and glue, and will strike on any surface. 'Safety' matches have heads containing potassium chlorate, potassium dichromate, red lead and antimony sulphide. They will ignite only when rubbed on a specially prepared surface containing red phosphorus.
3. Calcium orthophosphate (ground up) and superphosphate are fertilizers.
4. Phosphates are often used in medicines (tonics). Phosphorus is essential for healthy bones and teeth and for the functioning of nerves; foods containing the element in the combined state are milk, cheese, and green vegetables. Phosphates play an important part in the function of vitamins.
5. Complex phosphates are often used in water-softeners (e.g. Calgon). They 'trap' or sequester the troublesome Ca^{++} and Mg^{++} ions in solution, and do not allow them to perform their normal (disadvantageous) function.

11.7 QUESTIONS

1. What is the chief source of phosphorus? How is the element obtained commercially?

Give, in tabular form, a comparison of white and violet (or red) phosphorus.

2. Explain the meaning of the term allotropy. What would be your evidence that white and violet phosphorus are both forms of the same element?

3. Starting with white phosphorus, how would you obtain (*a*) red phosphorus, (*b*) phosphine, (*c*) orthophosphoric acid, (*d*) phosphorus trichloride, (*e*) phosphorus pentachloride?

4. Describe the preparations of the chlorides of phosphorus. How does each one react with water?

12 Silicon, Silica and Glass

12.1 SILICON

Occurrence and manufacture of silicon

Silicon occurs as silicon dioxide SiO_2 and silicates. It is the second most abundant element in the Earth's crust. It can be obtained by reduction of the oxide with hot carbon or a metal high in the electrochemical series, for example:

$$SiO_2 + 2Mg \rightarrow 2MgO + Si$$

Some magnesium silicide Mg_2Si is also formed.

Purer silicon is obtained by reduction of silicon tetrachloride with hot sodium or magnesium.

$$SiCl_4 + 4Na \rightarrow Si + 4NaCl$$

Unlike carbon (also in Group IVB of the Periodic Table) it exists in only one form, having a structure like that of diamond (fig. 10.1).

Properties of silicon

Finely divided silicon burns in air or oxygen.

$$Si + O_2 \rightarrow SiO_2$$

Common mineral acids have no effect on it. It decomposes steam at red heat.

$$Si + 2H_2O \rightarrow SiO_2 + 2H_2$$

With warm fairly concentrated sodium hydroxide solution it gives sodium silicate and hydrogen.

$$Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2$$

or

$$Si + 2OH^- + H_2O \rightarrow SiO_3^{--} + 2H_2$$

Uses of silicon

The main use of the element is in silicon steels.

12.2 SILICA SiO_2

Silica is very abundant, occurring as quartz, flint, and in sand (coloured by impurities such as ferric oxide). It also occurs in many rocks such as granite, and in clay as a hydrated aluminium silicate,

$$Al_2O_3 . 2SiO_2 . 2H_2O$$

Pure silica is a transparent solid, harder than glass, m.p. 1500°C. It can be fused and worked giving a glass-like substance, silica glass, having a very small coefficient of expansion (which can therefore withstand sudden changes of temperature).

Silica is an acidic oxide. It does not react directly with water but combines with solutions of caustic alkalis forming silicates.

$$SiO_2 + 2OH^- \rightarrow SiO_3^{--} + H_2O$$

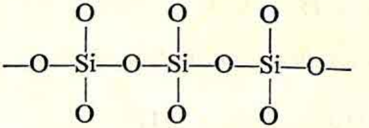
When fused with sodium carbonate, a glassy mass of sodium silicate is formed (cf. manufacture of phosphorus, where silica ejects phosphorus pentoxide).

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2\uparrow$$

A concentrated solution of sodium silicate in water is 'water glass', used for preserving eggs.

When reacted with dilute hydrochloric acid, sodium silicate gives sodium chloride and silicic acid (these can be separated by dialysis, see 14.4).

Unlike carbon dioxide, silica has a giant molecular structure containing covalent bonding. This gives it the property of being a solid, whereas carbon dioxide is a gas.



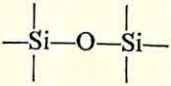
$$\begin{array}{ccccccc} & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & \\ & | & & | & & | & \\ \text{—O—} & \mathrm{Si} & \text{—O—} & \mathrm{Si} & \text{—O—} & \mathrm{Si} & \text{—O—} \\ & | & & | & & | & \\ & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & \end{array}$$

(in 3-dimensions)

The oxygen atoms are arranged tetrahedrally around the silicon atoms.

Silicones

Silicones are polymers (see 10.3) that have alternate silicon and oxygen atoms and have organic groups attached to the silicon atoms. The siloxane unit,



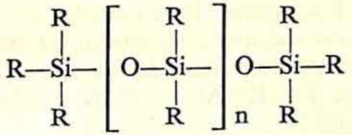
$$\begin{array}{ccccc} & | & & | & \\ \text{—} & \mathrm{Si} & \text{—O—} & \mathrm{Si} & \text{—} \\ & | & & | & \end{array}$$

gives the molecule stability towards heat (cf. silica). The organic groups control properties such as solubility in organic solvents, flexibility, water-repellency, etc. Silicons are made, for example, by hydrolysis of a chlorosilane, for example:

$$\begin{array}{r} \underset{\substack{\text{methyl}\\ \text{chloride}}}{2CH_3Cl} + Si \rightarrow \underset{\text{chlorosilane}}{(CH_3)_2SiCl_2} \xrightarrow{\text{hydrolysis}} (CH_3)_2Si(OH)_2 \\ \downarrow \text{polymerization} \qquad \\ \text{silicone} \qquad\qquad\quad \end{array}$$

Silicones can be divided into 3 types, the properties depending upon the structure.

1. *Fluids*—long chain polymers



$$R-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-\left[O-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-\right]_n O-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-R \quad (R = \text{organic group})$$

They are used in polishes, paints, for water-proofing paper, fabrics, and leather. They have anti-foaming properties and are used to suppress foaming of detergents in sewage disposal units.

2. *Rubbers*—the chains here are 'cross-linked'. They are more stable at low temperatures (ca. −70°C) and high temperatures (200–300°C) than ordinary rubbers, more resistant to chemical attack, but have inferior strength.

3. *Resins*—three-dimensional structures (cf. SiO_2). They are usually applied as solutions in organic solvents and are used as an electrical insulating varnish or for water-repellancy.

12.3 GLASS

In making glass, a mixture of silicates of two or more metals is fused and carefully cooled. The result is not a true solid, but a supercooled liquid which gets stronger as it cools, eventually attaining the strength and rigidity of a crystalline solid. When heated, it does not melt at a fixed temperature but softens over a definite range, so that it can be blown and drawn out into various shapes.

Ordinary window glass is a mixture of silicates of sodium, calcium and lead and is obtained by fusing together a mixture of sodium carbonate, sand, chalk, and a small quantity of lead monoxide. For hard glass (chemical apparatus, etc.) potassium carbonate is used instead of the sodium compound.

Flint glass (e.g. for lenses and prisms) contains lead monoxide instead of calcium oxide, and has a high refractive index.

Glasses with heat-resisting properties, e.g. Pyrex, Hysil, have low coefficients of expansion and can withstand rapid changes of temperature without fear of cracking. They contain a much higher silica content than ordinary glass and also contain borates, this being achieved by addition of borax ($Na_2B_4O_7 . 10H_2O$) to the melt.

Coloured glasses are made by addition of various metallic oxides to the melt, e.g. cobalt oxide gives blue, chromic oxide gives green.

12.4 SILICATES

These are the salts of silica, when reacted with bases. Since there are many complex silicic acids, silicates often have complex crystal structures. They can be both natural and artificial. Silicates, together with quartz and clay, are present in common rocks. In granite, for example, quartz is present with micas, e.g. $K^+(Al^{+++})_3[Si_3O_{10}(OH)_2]^{10-}$ and Felspars, e.g. $K^+Al^{+++}[Si_3O_8]^{4-}$.

When rocks like granite are 'weathered', clays and shales are formed. These also consist of a mixture of silicates. Soil is a product of the disintegration of rocks and also contains decaying animal and vegetable matter (humus).

Asbestos is a complex silicate containing Ca^{++} and Mg^{++} ions and exists as a fibrous solid. It is used to make fireproof clothing, electrical insulation, boiler covers, and as a building material, etc.

Sodium zeolite is an artificial complex silicate with ion-exchange properties (see 7.11).

12.5 CEMENT

Cement is essentially calcium aluminium silicate. It is made by heating powdered 'marl', a natural mixture of limestone and clay, about two-thirds limestone to one-third clay. Marl is crushed, made into a slurry with water, and sintered in a rotating cylindrical container heated by burners at the lower end (burning coal or oil).

When water is added, a gel is first formed which then slowly crystallizes to a hard solid. This setting is a complex process, but examination of the setting with an electron microscope at a magnification of 20,000 has revealed that long needle-like crystals form throughout the mass of the material, giving it hardness and strength. It is called Portland cement, since the hard mass resembles Portland stone. When mixed with gravel, it gives *concrete*.

12.6 QUESTIONS

1. Adduce evidence that silica is an acidic oxide. How would you prepare silicic acid?
2. Compare and contrast the physical and chemical properties of silica and carbon dioxide.
3. Write an essay on 'glass'.

13 The Halogens

13.1 INTRODUCTION

This family (the 'salt-producers') contains fluorine, chlorine, bromine, iodine, and astatine (radioactive). Their general properties have been outlined in 2.12.

13.2 OCCURRENCE AND PREPARATION OF CHLORINE

Chlorine occurs as metallic chlorides, e.g. Na^+Cl^- (in Rock salt, sea water), K^+Cl^- (in Carnallite $KCl.MgCl_2.6H_2O$), $Ca^{++}(Cl^-)_2$ (in sea water).

It is prepared by oxidation of the chloride ion in concentrated hydrochloric acid with potassium permanganate (no heat required) or manganese dioxide (heat required).

$$2MnO_4^- + 16H^+ + 10Cl^- \rightarrow 2Mn^{++} + 8H_2O + 5Cl_2\uparrow$$
$$MnO_2 + 4HCl \rightarrow 2H_2O + Mn^{++} + 2Cl^- + Cl_2\uparrow$$

(Construct these equations from the oxidizing and reducing equations as demonstrated in chapter four.)

It is dried by concentrated sulphuric acid and collected by downward delivery (or sometimes 'over brine').

Preparation of chlorine

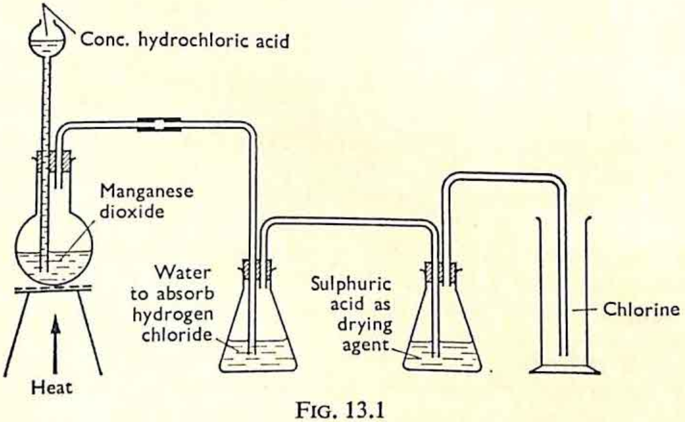

Conc. hydrochloric acid
Manganese dioxide
Water to absorb hydrogen chloride
Sulphuric acid as drying agent
Chlorine
Heat

FIG. 13.1

Chlorine is obtained commercially as a co-product of the electrolysis of brine in the Castner-Kellner cell (3.4), or as a by-product of the manufacture of some metals, e.g. sodium, calcium.

13.3 PROPERTIES OF CHLORINE

It is a greenish-yellow gas with a pungent smell and is very poisonous. It is used for sterilizing drinking water and for killing bacteria in swimming pools. Moist bleaching powder $CaO.Cl_2$ (this is a simplified formula), which gives chlorine when reacted with any dilute acid (even carbonic acid in the air), is used for many sanitary purposes.

Chlorine is easily liquefied. It is heavier than air. It is soluble in water to give 'chlorine water' from which crystals of chlorine hydrate $Cl_2.xH_2O$ (where $x = 6$–8) are obtained on cooling. These crystals give chlorine when heated.

Chlorine also reacts with water.

$$Cl_2 + H_2O \rightarrow HCl + \underset{\text{hypochlorous acid}}{HOCl}$$

On standing, hypochlorous acid slowly decomposes.

$$2HOCl \rightarrow 2HCl + O_2\uparrow$$

Chlorine is a vigorous oxidizing agent when water is present, many of its oxidizing properties being attributed to hypochlorous acid.

$$OCl^- + 2H^+ + 2e \rightarrow Cl^- + H_2O$$

For example: sulphite ions are oxidized to sulphate ions.

$$SO_3^{--} + H_2O - 2e \rightarrow SO_4^{--} + 2H^+$$

that is $$SO_3^{--} + OCl^- \rightarrow Cl^- + SO_4^{--}$$

Chlorine can also act as an oxidizing agent by removal of hydrogen atoms.

$$Cl_2 + 2[H] \rightarrow 2HCl$$

For example:

$$\underset{\substack{\text{turpentine}\\\text{(warm)}}}{C_{10}H_{16}} + 8Cl_2 \rightarrow 10C + 16HCl$$

$$H_2S + Cl_2 \rightarrow S + 2HCl$$

Chlorine can also oxidize by removal of electrons, since it is highly electronegative (2.11), for example:

$$2Fe^{++} + Cl_2 \rightarrow 2Fe^{+++} + 2Cl^-$$

$2I^- + Cl_2 \rightarrow I_2 + 2Cl^-$ (chlorine turns starch-iodide paper blue)

N.B. Chlorine oxidizes bromide and iodide ions to the free halogens. Bromine, a weaker oxidizing agent, only oxidizes iodide ions, while iodine (an even weaker oxidizing agent) does not oxidize any halide ions (except astatide ions).

If a piece of filter paper dipped in potassium iodide solution is held in chlorine vapour, the paper will turn brown owing to the iodine displaced; this is a useful test for chlorine.

Moist chlorine is used as a bleaching agent, owing to the presence of hypochlorous acid. Many coloured substances can be oxidized by this, forming colourless ones. Moist litmus is first turned red by the gas and is then bleached, this also being a test for chlorine. Commercially, moist chlorine is used to bleach fabrics such as cotton, linen and also paper. The article is washed well with water after bleaching, since hydrochloric acid is formed.

Chlorine reacts with most other elements forming chlorides. Thus, it oxidizes metallic elements forming, in general, ionic chlorides, the ease of reaction decreasing with decreasing position of the metal in the electrochemical series. It also reacts with non-metals, forming covalent chlorides.

Where the metal forms more than one chloride, the one where the metal is in its highest valency state (oxidation state) is formed, for example:

$$2Fe + 3Cl_2 \xrightarrow{\text{heat}} 2FeCl_3 \quad \text{(anhydrous ferric chloride)}$$

(cf. hydrogen chloride reacts with hot iron to give anhydrous ferrous chloride).

Preparation of anhydrous ferric chloride

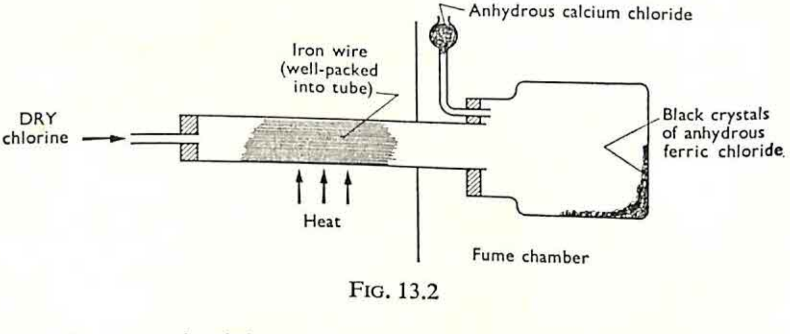

Anhydrous calcium chloride
Iron wire (well-packed into tube)
DRY chlorine
Black crystals of anhydrous ferric chloride
Heat
Fume chamber

FIG. 13.2

Anhydrous aluminium chloride can be made using the same type of apparatus.

Chlorine does not combine directly with oxygen, nitrogen, carbon or Rare Gases.

Chlorine reacts with solutions of alkalis, the product depending on the conditions.

(*a*) Cold, dilute alkali in excess

$$2OH^- + Cl_2 \rightarrow \underset{\substack{\text{hypochlorite}\\\text{ion}}}{OCl^-} + Cl^- + H_2O$$

(*b*) Hot, conc. alkali, excess chlorine

$$6OH^- + 3Cl_2 \rightarrow 5Cl^- + \underset{\substack{\text{chlorate}\\\text{ion}}}{ClO_3^-} + 3H_2O$$

(this equation is built up as described in 3.4).

13.4 HYDROGEN CHLORIDE HCl

Preparation

Hydrogen and chlorine combine explosively in the sunlight, and this is not, therefore, a convenient preparation.

$$H_2 + Cl_2 \rightarrow 2HCl$$

Rock salt is heated with concentrated sulphuric acid.

$$Na^+Cl^- + \overbrace{2H^+ + SO_4^{--}} \rightarrow \overbrace{Na^+ + HSO_4^-} + HCl\uparrow$$

The gas is collected by downward delivery, being heavier than air (or dried by concentrated sulphuric acid and collected over mercury, but this is seldom used in schools).

Commercially, it is made by burning hydrogen in chlorine at a special jet, or reacting the gases in the presence of a catalyst. Both gases are obtained by electrolysis of concentrated brine (see 3.4).

The older method was to heat Rock salt with concentrated sulphuric acid at a temperature higher than that used in the laboratory preparation.

$$2Na^+Cl^- + H_2SO_4 \rightarrow \overbrace{2Na^+ + SO_4^{--}} + 2HCl$$

Properties

It is a colourless gas with a choking smell and acid taste. It is heavier than air, easily liquefied, and is very soluble in water (the fountain experiment can be performed with it, cf. ammonia, nitrogen dioxide; fig. 4.5). It is a covalent compound (H—Cl), but hydrochloric acid, which is formed when the gas dissolves in water, is ionic (and therefore a strong electrolyte) since it contains hydroxonium and chloride ions (H_3O^+, Cl^-). When hydrogen chloride is passed into water in the laboratory preparation of hydrochloric acid, some type of device, e.g. a funnel, is needed to prevent 'sucking back'.

Preparation of hydrogen chloride and hydrochloric acid

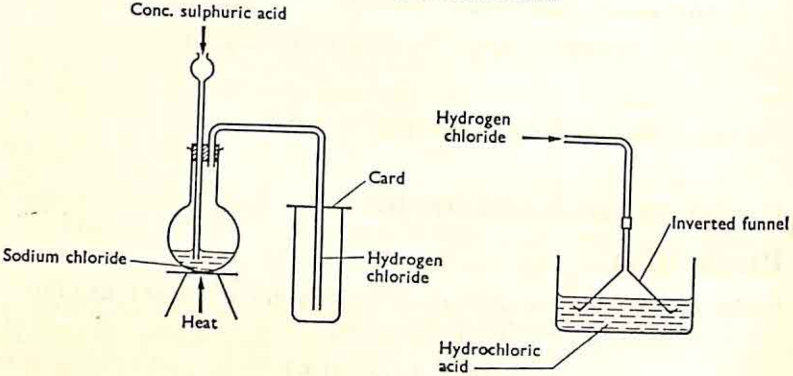


FIG. 13.3

One volume of water at 0°C dissolves about 500 volumes of hydrogen chloride.

Hydrogen chloride fumes in moist air. It forms a constant boiling mixture with water containing 20·24 per cent hydrogen chloride and b.p. 110°C. If dilute hydrochloric acid is distilled, water vapour escapes until the constant boiling mixture is reached. If concentrated hydrochloric acid is distilled, hydrogen chloride fumes escape until, eventually, the constant boiling mixture is again reached.

Hydrogen chloride is very poisonous.

When hydrogen chloride comes into contact with ammonia vapour, white fumes of ammonium chloride are formed. This is what happens when a bottle of concentrated hydrochloric acid is opened near a bottle of 0·88 ammonia.

$$NH_3 + HCl \rightarrow NH_4^+Cl^-$$

If hydrogen chloride is passed into silver nitrate solution, a white precipitate of silver chloride is formed.

$$HCl + Ag^+ \rightarrow AgCl\downarrow + H^+$$

Hydrochloric acid is a strong monobasic acid, forming salts (chlorides), for example:

(*a*) $Zn + 2H^+ + 2Cl^- \rightarrow Zn^{++} + 2Cl^- + H_2$
(*b*) $CuO + 2H^+ + 2Cl^- \rightarrow Cu^{++} + 2Cl^- + H_2O$
(*c*) $Na^+ + OH^- + H^+ + Cl^- \rightarrow Na^+ + Cl^- + H_2O$

(a solution of sodium hydroxide is used here)

(*d*) $(Na^+)_2CO_3^{--} + 2H^+ + 2Cl^- \rightarrow 2Na^+ + 2Cl^- + H_2O + CO_2\uparrow$

Chlorides are generally crystalline salts containing ionic bonds, e.g. Na^+Cl^-. They have varying numbers of molecules of water of crystallization. Most chlorides are soluble in water, except AgCl, $PbCl_2$, CuCl and Hg_2Cl_2. Lead chloride is *much* more soluble in hot water than in cold.

The test for chlorides are as follows:

1. With concentrated sulphuric acid they give hydrogen chloride gas.
2. When mixed with manganese dioxide and warmed with concentrated sulphuric acid they give chlorine.
3. In solution, they give a white precipitate of silver chloride when reacted with silver nitrate solution, the precipitate being discoloured in the light owing to reduction to silver. The precipitate is insoluble in dilute nitric acid but soluble in dilute ammonia solution (to give $Ag(NH_3)_2^+$ ions).

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow$$

Preparation of anhydrous chlorides

They cannot always be obtained by evaporation of the solutions, owing to hydrolysis, for example:

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl\uparrow$$

(*a*) Heat the metal in dry chlorine or dry hydrogen chloride, for example:

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3 \quad \text{(ferric chloride)}$$
$$2Al + 3Cl_2 \rightarrow 2AlCl_3$$
$$Fe + 2HCl \rightarrow FeCl_2 + H_2\uparrow \quad \text{(ferrous chloride)}$$

(*b*) Heat the oxide, mixed with carbon, in chlorine, for example:

$$Al_2O_3 + 3C + 3Cl_2 \rightarrow 2AlCl_3 + 3CO$$
$$Cr_2O_3 + 3C + 3Cl_2 \rightarrow 2CrCl_3 + 3CO$$

(the carbon is needed to rupture the strong metal/oxygen bond).

Uses of hydrochloric acid

It is used for cleaning metal surfaces before galvanizing, etc, as a general reagent, and in the ceramics, dyestuffs, and textiles industries.

Bleaching powder

This is formed when chlorine reacts with damp solid calcium hydroxide.

$$Cl_2 + Ca(OH)_2 \rightarrow CaO.Cl_2 + H_2O$$

It really has a much more complicated formula,

$$Ca(OCl)_2 + CaCl_2.Ca(OH)_2.H_2O$$

It is a white powder which gives off chlorine when reacted with dilute acids.

$$CaO.Cl_2 + 2H^+ \rightarrow Ca^{++} + H_2O + Cl_2$$

When heated with a solution of cobaltous nitrate (catalyst) oxygen is evolved.

$$2CaO.Cl_2 \rightarrow 2CaCl_2 + O_2$$

13.5 OCCURRENCE AND MANUFACTURE OF BROMINE

Bromine occurs as bromide ions in the bromides of Na, K, Mg, present in chloride deposits. The bromides remain in solution after the chlorides have been crystallized out. Bromides are present in sea water. If a very concentrated sample of sea water is electrolysed, a yellow colour (bromine) appears at the anode.

Bromine is manufactured from sea water by displacing it with chlorine.

$$2Br^- + Cl_2 \rightarrow 2Cl^- + Br_2$$

Provided the bromine is present in fairly large quantity, it can be volatilized in steam and condensed to a liquid.

Bromine can be prepared in the laboratory by warming potassium bromide with manganese dioxide and concentrated sulphuric acid.

$$2Br^- + MnO_2 + 3H_2SO_4 \rightarrow Mn^{++} + SO_4^{--} + 2HSO_4^- + Br_2\uparrow + 2H_2O$$

Preparation of bromine or iodine

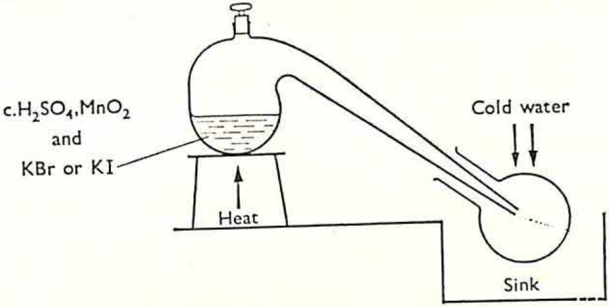


FIG. 13.4

13.6 PROPERTIES OF BROMINE

Bromine is a heavy red liquid with a pungent odour, very poisonous, and easily vaporized. The liquid burns the skin and the vapour attacks the eyes and nose.

It is slightly soluble in water (forming bromine water, from which crystals of the hydrate can be obtained) and is much more soluble in organic solvents, e.g. chloroform, carbon tetrachloride, carbon disulphide. The vapour is diatomic Br_2.

Bromine has chemical reactions similar to those of chlorine, but is less reactive. Thus, it combines readily with hydrogen only when heated.

$$H_2 + Br_2 \rightarrow 2HBr$$

It combines with phosphorus and metals only when heated, for example:

$$2P + 3Br_2 \rightarrow 2PBr_3$$
$$2Fe + 3Br_2 \rightarrow 2FeBr_3{}^*$$

It displaces iodine from iodides, but not chlorine from chlorides.

$$Br_2 + 2I^- \rightarrow I_2 + 2Br^-$$

The reaction with alkalis is analogous to that of chlorine, i.e. to give a hypobromite or bromate according to the conditions.

Bromine water bleaches, but less vigorously, than chlorine water.

Bromine is used in the manufacture of certain drugs, in the manufacture of potassium bromide used in medicine and photography, and in the manufacture of ethylene dibromide $C_2H_4Br_2$ (10.6); this is added to petrol to remove lead tetra-ethyl, 'antiknock', as *volatile* lead tetrabromide $PbBr_4$ (covalent).

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* Some ferroso ferric bromide, Fe_3Br_8, is also formed here.

13.7 OCCURRENCE AND MANUFACTURE OF IODINE

Iodine occurs as iodides in sea water (certain seaweed absorbs the iodides), and as iodates (particularly $NaIO_3$) in Chile saltpetre ('caliche').

It is manufactured as follows:

(*a*) 'Kelp', the ash from burnt seaweed contains potassium iodide, and this is extracted with water and heated with manganese dioxide and concentrated sulphuric acid.

$$2I^- + MnO_2 + 3H_2SO_4 \rightarrow Mn^{++} + SO_4^{--} + 2HSO_4^- + I_2 + 2H_2O$$

(*b*) After sodium nitrate has been crystallized out from Chile saltpetre, sodium iodate (more soluble) is left in the 'mother liquor'. This is reduced to iodine with sodium bisulphite.

$$2IO_3^- + 5HSO_3^- \rightarrow 3HSO_4^- + I_2 + H_2O + 2SO_4^{--}$$

Iodine is purified by sublimation.

It is prepared in the laboratory by oxidation of iodide ions in potassium iodide, by heating it with manganese dioxide and concentrated sulphuric acid.

13.8 PROPERTIES OF IODINE

Iodine is a black lustrous crystalline solid which readily sublimes to a violet vapour I_2. If heated strongly, this dissociates $I_2 \rightleftharpoons 2I$. It is only very slightly soluble in water, but is soluble in many organic solvents; with those containing oxygen atoms it gives a brown colour (e.g. alcohols, ethers), while with those not containing oxygen atoms it gives a violet colour (e.g. chloroform, carbon disulphide).

It dissolves readily in potassium iodide solution forming potassium tri-iodide.

$$I_2 + I^- \rightleftharpoons \underset{\text{complex ion (deep red)}}{I_3^-}$$

With a solution of starch it gives an intense blue colour (test for iodine or starch).

It is less reactive than bromine. It combines with hydrogen on heating, but the reaction is reversible.

$$H_2 + I_2 \rightleftharpoons 2HI$$

It combines with many metals forming iodides and also reacts with many non-metals on warming, for example:

$$2Na + I_2 \rightarrow 2NaI \text{ (i.e. } 2Na^+I^-\text{)}$$
$$2P + 3I_2 \rightarrow 2PI_3$$

It is less powerful as an oxidizing agent than bromine or chlorine. It is not a bleaching agent.

With sodium thiosulphate, it gives sodium tetrathionate.

$$I_2 + 2S_2O_3^{--} \rightarrow S_4O_6^{--} + 2I^-$$

Chlorine and bromine behave differently, for example:

$$4Cl_2 + 5H_2O + S_2O_3^{--} \rightarrow 8Cl^- + 10H^+ + 2SO_4^{--}$$

It does not displace chlorine or bromine from solution.

The reaction with alkalis is similar to that of chlorine and bromine, although the hypoiodite, e.g. NaOI, is much less stable than the hypochlorite or hypobromite.

$$3NaIO \rightarrow NaIO_3 + 2NaI \quad \text{(slowly, room temperature)}$$

Uses of iodine include 'tincture of iodine' (iodine and potassium iodide dissolved in alcohol and water, used in medicine), and as essential element to health (deficiency causes diseases of the thyroid gland, e.g. goitre).

13.9 HYDROGEN BROMIDE AND HYDROGEN IODIDE

These cannot be made by reacting an iodide with concentrated sulphuric acid since this would oxidize (at least partially) the hydrogen halide to the free halogen, for example:

$$2HBr + H_2SO_4 \rightarrow Br_2 + 2H_2O + SO_2$$

To make hydrogen bromide, liquid bromine is dropped on to a paste of red phosphorus and water and the gas evolved passed through a tube of moist red phosphorus to remove any bromine still present.

$$2P + 3Br_2 \rightarrow 2PBr_3$$
$$PBr_3 + 3H_2O \rightarrow H_3PO_3 + 3HBr$$

For hydrogen iodide, water is dropped on to a paste of red phosphorus and iodine.

Preparation of hydrogen bromide

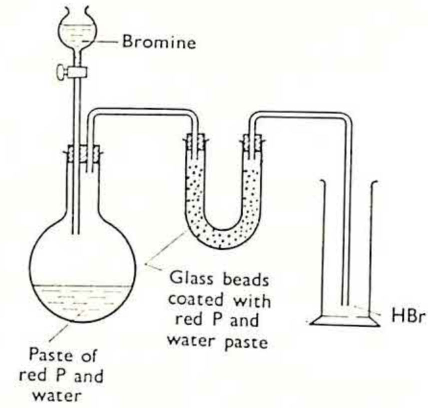

FIG. 13.5

Alternatively, potassium bromide or iodide can be reacted with orthophosphoric acid (not a powerful oxidizing agent), for example:

$$I^- + H_3PO_4 \rightarrow HI\uparrow + H_2PO_4^-$$

Preparation of hydrogen iodide

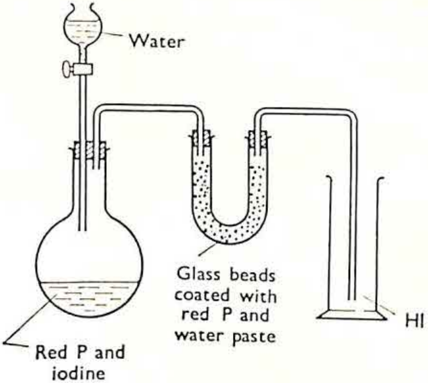

FIG. 13.6

Both compounds are colourless gases which fume in moist air. They are covalent. They form constant boiling mixtures with water (47% HBr, b.p. 125°C and 57% HI, b.p. 127°C). They are very soluble in water (a funnel is used in the preparation of the acids to prevent 'sucking back').

The acids are easily oxidized in the air, turning yellow or brown, for example:

$$\overbrace{4H^+ + 4I^-} + O_2 \rightarrow 2H_2O + 2I_2$$

Hydrogen iodide is a powerful reducing agent and is often used as such in organic chemistry.

Tests for bromide and iodide ions in solution

To the solution, silver nitrate is added. A cream precipitate, insoluble in dilute nitric acid but partially soluble in dilute ammonia solution, is silver bromide $AgBr$. A yellow precipitate, insoluble in both reagents, is silver iodide AgI.

Alternatively, if chlorine water is added to the solution, bromine or iodine is liberated. If carbon tetrachloride (or chloroform) is added and the liquid shaken, a brown colour in the organic layer shows the presence of bromine while a violet colour shows iodine.

13.10 QUESTIONS

1. Give a brief comparative account (preferably in tabular form) of the chemistry of chlorine, bromine and iodine, and their hydrides.
2. How may hydrogen chloride be prepared in the laboratory? Why are hydrogen bromide and hydrogen iodide made differently?
3. Use your knowledge of the principles of the Periodic Table to predict some features in the chemistry of astatine?
4. What are the tests for chloride, bromide and iodide ions in solution?
5. Give an account of the preparation of chlorine. How, and under what conditions, does it react with (*a*) sodium hydroxide, (*b*) hydrogen sulphide, (*c*) potassium bromide, (*d*) water, (*e*) sulphur dioxide, (*f*) iron?

   What is a test for chlorine?
6. Describe the manufacture of (*a*) chlorine, (*b*) iodine.
7. What tests would you carry out in order to ascertain whether a given gas was bromine vapour or nitrogen dioxide? Calculate the weight of 1 litre of each gas at N.T.P.
8. Describe what you would see when each of the following salts is heated with concentrated sulphuric acid: sodium chloride, sodium bromide, sodium iodide. How would you prepare hydrobromic acid?

14 Solutions and Related Topics

14.1 DEFINITIONS

A *solution* is a homogeneous (same throughout) mixture of two or more substances.

The substance dissolved is called the *solute*.

The substance which carries out the dissolving is called the *solvent*.

In general, the solute is the substance present in least quantity while the solvent is that present in greater quantity.

Solutions of solids in liquids are most common, although there can be solutions of gases in gases, gases in liquids, liquids in liquids, solids in solids, etc. The dissolved particles cannot be seen either with the naked eye or with a microscope.

When talking about solutions, it is important to specify the solvent as well as the solute. Thus, sugar dissolves in water but not in carbon disulphide. Sulphur is insoluble in water but is soluble in carbon disulphide. In general a solute dissolves in a solvent which has a similar chemical nature. Thus methane dissolves in a hydrocarbon solvent such as benzene but not in water. Sodium chloride dissolves in water but not in benzene.

Water is a polar solvent, i.e. the molecules of water are partially ionic owing to the difference in electronegativity between hydrogen and oxygen (2.11). It is not surprising, therefore, that it dissolves many ionic substances but not many covalent ones. The ability of water to dissolve ionic substances depends upon (*a*) the ability of water to weaken the forces holding the ions together, (*b*) the ability of water to *hydrate* the separated ions, thus releasing energy (the energy of hydration) needed to complete the solution. When covalent compounds dissolve in water, it is generally with the attendant formation of hydrogen bonds with water molecules (2.16).

We know that there is an energy change when a substance changes its phase. Is there an energy change involved in solution? You can study heats of solution by dissolving 0·1 g-formula weight of a substance (e.g. $Na_2S_2O_3$, NaOH, NH_4Cl) in 100 cm^3 of water in a polythene bottle and measuring the temperature change.

A *suspension* is a heterogeneous (different throughout) mixture formed when a solid is added to a liquid (fluid) in which it is not soluble. For example, sulphur forms a suspension in water and sugar forms a suspension in carbon disulphide. A suspension differs from a solution in that:

1. visible particles are present
2. the solid particles *sediment* under gravity to the bottom of the container
3. the suspended particles can be removed by filtration (see 1.6)

Colloidal solutions are those in which the size of the particles is intermediate between those in true solutions and in suspensions. The colloidal particles cannot be seen with the naked eye, but they are large enough to scatter light incident on them, this being the basis for viewing them with an ultramicroscope.

A *saturated solution* is one which contains as much dissolved solid as the solvent can possibly dissolve at the given temperature in the presence of excess solid. Its composition is fixed at a given temperature.

Solubility curves

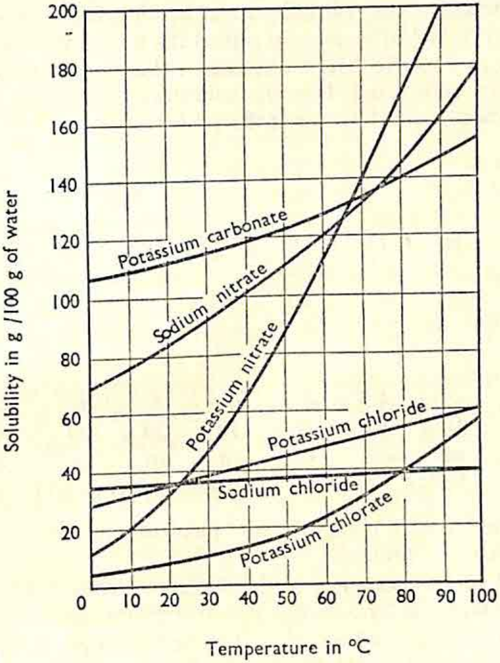

FIG. 14.1

The *solubility* of a solute in a solvent at a given temperature is the number of grams of solute which is required just to give a true saturated solution when 100 g of solvent are used.

The solubility of a solid in a liquid generally rises as the temperature rises. If this variation is represented graphically, the graph is called a *solubility curve*. One example of a substance for which the solubility decreases with rise of temperature is calcium hydroxide.

Since a solid dissolves in its almost saturated solution with the absorption of heat, it follows (by Le Chatelier's principle) that the solubility of a solid in a liquid increases with rise of temperature.*

To plot a solubility curve for potassium chlorate

Weigh 4·5 g of the solid into a boiling tube and add 10 cm^3 of distilled (or deionized) water from a burette. Heat the tube until the solid has dissolved. Allow the solution to cool and stir it constantly (with a thermometer). Note the temperature at which crystals begin to form. At this temperature, the solubility must be 45 g/100 g of water (why?). Add a further 3 cm^3 of water and repeat the determination by allowing the solution to cool further. Continue in this way until the following table has been completed. Plot the solubility against the temperature, drawing a smooth curve through the points.

Total weight of water present (in grams)	10	13	16	19	24	29	39	49
Temperature at which crystals just appear								
Solubility at this temperature	4·5 g/ 10 g of water	4·5 g/ 13 g of water	4·5 g/ 16 g of water	4·5 g/ 19 g of water	4·5 g/ 24 g of water	4·5 g/ 29 g of water	4·5 g/ 39 g of water	4·5 g/ 49 g of water

After completing the experiment, measure the volume of solution with a measuring cylinder.

Comment on the accuracy of the determinations.

A *supersaturated solution* is one which contains more dissolved solute than does a true saturated solution. The best example is 'hypo', sodium thiosulphate, $Na_2S_2O_3.5H_2O$, which dissolves in its own water of crystallization on heating. On cooling, a supersaturated solution is formed which only crystallizes (with the liberation of heat, due to hydration of the crystals) on the addition of a crystal of hypo, an isomorphous (same shape) substance, or dust.

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* The solubility of a gas in water generally decreases as the temperature rises—air can be expelled from water by boiling it.

14.2 MEASUREMENT OF SOLUBILITY OF A SOLID IN A LIQUID

(*a*) Make a saturated solution, keep it in a thermostat, and allow it to 'settle'.

(*b*) Remove a volume of this solution with a pipette fitted with a filter (to trap solid particles, and pre-heated to the temperature of the thermostat if this is above room temperature) and transfer it to a weighed evaporating basin. Find the weight.

(*c*) Evaporate the solution carefully to dryness (using a water-bath and drying oven) and reweigh to find the weight of solute.*

(*d*) Calculate the weight of solute dissolved per 100 g of solvent.

14.3 CRYSTALS, ETC

Solids can be either crystalline (definite geometrical shape) or amorphous (no definite shape). A *crystal* is a homogeneous solid bounded by severally naturally-occurring plane faces. Crystals can be characterized by their shapes. Larger crystals can be 'grown' from smaller ones, while still preserving their shape, by suspending them for some time in a saturated solution of the material.

Allotropy is the existence of an element in several crystalline forms in the same state. Polymorphism is the existence of a compound in several forms in the same state, e.g. $CaCO_3$ (calcite, aragonite), HgI_2 (red, yellow).

Crystals can be obtained by (*a*) cooling hot saturated solutions or allowing cold saturated solutions to evaporate, (*b*) allowing a molten solid (e.g. a metal) to solidify, (*c*) by subliming a solid.

If a molten metal is mixed with another molten element, it is often found, on cooling, that a mixture called an *alloy* is formed, e.g. brass (copper/zinc), bronze (copper/tin), steel (iron/carbon/other elements).

Some examples of amorphous substances are pitch and glass.

A crystalline substance has a definite melting point whereas an amorphous substance does not.

14.4 COLLOIDS

The nature of the colloidal state has been outlined in 14.1. The colloidal particles can be seen only with an ultramicroscope, which relies on the scattering of light by the particles (Tyndall effect). The scattered light can be viewed with a travelling microscope, or examined directly (when it is seen as a thick wedge).

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* Alternatively, the concentration of the solution can be estimated by a suitable titrimetric or gravimetric method.

Colloidal particles, when viewed by the ultramicroscope (using a travelling microscope), are seen to be in continual zig-zag motion (Brownian motion), this being due to bombardment of the particles by molecules in the medium in which they are dispersed (dispersion medium); the dispersed particles are referred to as the disperse phase.

The Tyndall effect

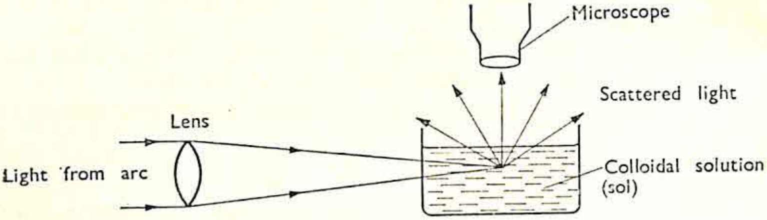


FIG. 14.2

There are several types of colloidal solution, according to the nature of the disperse phase and dispersion medium.

Table 14.1

Disperse phase	*Dispersion medium*	*Name*	*Example*
1. Liquid	Gas	Fog	Ordinary fog
2. Solid	Gas	Smoke	Ordinary wood or coal smoke
3. Gas	Liquid	Foam	Soap bubbles, 'Aero' chocolate (the liquid has solidified here)
4. Liquid	Liquid	Emulsion	Milk (butter fat dispersed in weak sugar solution)
5. Solid	Liquid	Sol	Starch sol, gelatine sol

Sols are the most important. When they are concentrated, they often set to gels (ordinary table jelly is a gel).

There is no rigid boundary between colloidal and true solutions, or colloidal solutions and suspensions. Thus a mud, or slime, is on the boundary between a colloid and a fine suspension of solid particles in a liquid medium.

Separation of colloids from particles in true solution can be effected by *dialysis*. The solution and the sol are placed in a special parchment bag (called a dialysis bag) which is then placed in a container of distilled water. The colloidal particles stay in the bag while the dissolved particles pass out into the water.

Dialysis

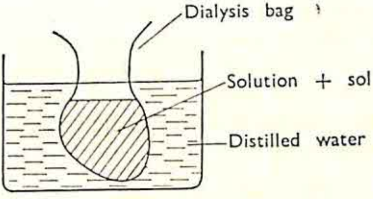


FIG. 14.3

Sols are of two types, lyophilic (solvent-loving, e.g. starch sol, albumin, gelatin) and lyophobic (solvent-hating, e.g. colloidal metals, ferric hydroxide sol). The latter have a much more pronounced Tyndall effect than the former, have a viscosity approximately the same as that of water (whereas the viscosity of lyophilic is generally much greater), and are irreversible—this means that, when evaporated to dryness, the sol cannot be regenerated by addition of water (lyophilic sols, however, are reversible—think of making a table jelly). Lyophobic sols can be coagulated (precipitated) by the additions of inorganic salts, whereas lyophilic sols cannot. Precipitation is normally prevented in a sol by the fact that all the colloidal particles in one type of sol bear the same electrical charge, thereby repelling one another. Addition of an ion of opposite charge neutralizes that on the colloidal particle, allowing the particles to unite into a precipitate. The coagulating power of an ion is greater the bigger the electrical charge, i.e. the larger the valency; this is called the Hardy-Schulze rule. It is for this reason that Al^{+++} ions are used (in the form of Alum) in treating sewage and in shaving (as a styptic pencil, which coagulates blood—a 'negative' colloid).

It is often found that a lyophilic sol can protect a lyophobic one from coagulation. For example, mayonnaise is an emulsion of oil in vinegar with an emulsifier of egg yolk. In many rivers, e.g. the river Nile, clay in colloidal solution is prevented from coagulation by organic matter. When the sea is reached, the high concentration of salts is able to cause coagulation, forming the 'muddy' delta.

14.5 QUESTIONS

1. Explain carefully the difference between melting and dissolving.

2. Comment on the following statement: ethanol is an organic liquid, and a covalent compound, and yet it is soluble in water.

3. Define solution, solute, solvent, solubility. How would you determine the solubility of potassium nitrate in water at 20°C?

4. Write briefly on (*a*) Colloids, (*b*) Suspensions, (*c*) Supersaturated solutions, (*d*) Saturated solutions, (*e*) Crystals.

5. 15 g of a solution at 25°C and 80°C, respectively left, on evaporation, 2·5 g and 5·0 g of solid. Find, and state correctly, the solubility of the solid at both temperatures. [20 g of solute per 100 g of solvent at 25°C.; 50 g of solute per 100 g of solvent at 80°C.]

6. 100 g of water dissolve the following weights of ammonium chloride at the temperatures named:

Temp. °C	0	10	20	30	40	50	60	80	100
Wt in g	28·4	32·8	37·3	41·3	46·2	50·6	55·0	64·0	72·8

Construct the solubility curve for the solid, and from this determine the solubility of ammonium chloride at 24°C and 70°C.

15 Equivalent, Atomic and Molecular Weights

15.1 EQUIVALENT WEIGHTS OF ELEMENTS

The equivalent weight of an element is the number of parts by weight of it which will combine with, displace, or otherwise play the same part as 1 part by weight of hydrogen, 8 parts by weight of oxygen, 35½ parts by weight of chlorine, or the equivalent weight of any other element.

[1-gram equivalent weight of an element evolves 11·2 l of hydrogen at N.T.P. 1-gram equivalent weight of an element reacts with 1 l of a normal solution (see chapter 17).]

15.2 DETERMINATION OF EQUIVALENT WEIGHTS

(a) By displacement of hydrogen

A known weight of metal is reacted with a suitable acid (e.g. zinc + dil. H_2SO_4, magnesium + dil. HCl or H_2SO_4, aluminium with dil. HCl, iron with conc. HCl, etc). The hydrogen evolved is collected over water at room temperature and the volume and atmospheric pressure recorded. In some cases, the metal can be reacted with an alkali (e.g. zinc + NaOH, Al with conc., warm NaOH) or an alcohol (e.g. Na or K with ethanol).

The apparatus for determining the equivalent weight of magnesium with dilute hydrochloric acid is shown in fig. 15.1.

After allowing reaction to proceed to completion,

$$Mg + 2H^+ \rightarrow Mg^{++} + H_2\uparrow$$

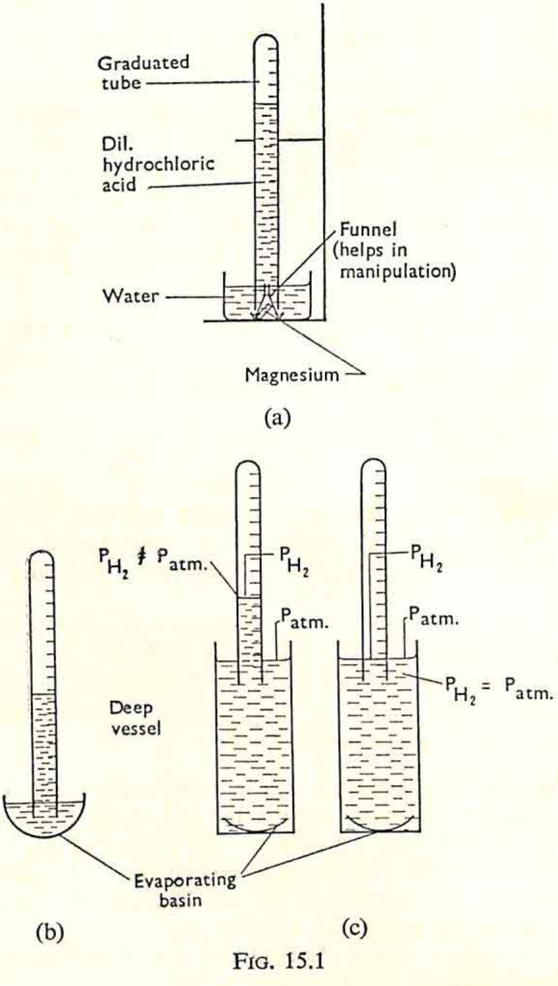
the hydrogen in the graduated tube is transferred, via an evaporating basin, to a deep vessel containing water and raised and lowered until the levels inside and outside are equal. The volume of gas is then being measured at atmospheric pressure, as recorded by a barometer.

Alternatively, the apparatus of fig. 15.2 can be used; a typical experiment could be performed as follows:

(*a*) Place a known weight of metal and a small test tube full of concentrated hydrochloric acid into flask A.

(*b*) Reconnect flask A. Raise the tube C till the level of water in it is several inches above the level in tube B. If the levels remain constant the apparatus must be airtight. If not, remedy the situation before proceeding.

(*c*) Now equalize the levels in tubes B and C. This ensures that the pressure inside the flask is atmospheric pressure. Read off the liquid level in tube B.



(a)

(b) (c)

FIG. 15.1

(*d*) Spill acid on to the metal in A by tilting the flask. As hydrogen is evolved and pushes the water level in B down run water out of the tap X at such a rate that the liquid levels in B and C remain approximately equal.

(*e*) When evolution of hydrogen ceases allow the apparatus to cool, equalize the levels in tubes B and C, and read the liquid level in B.

(*f*) Record the barometric pressure and the room temperature. Look up the value of the vapour pressure of water at this temperature.

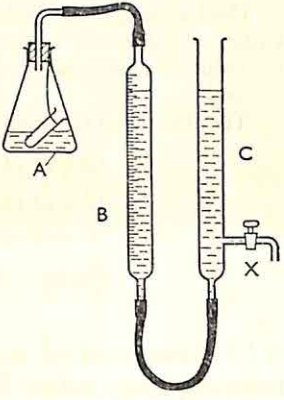


FIG. 15.2

Example. 0·160 g of a metal displaced 156 cm^3 of hydrogen under the above conditions, the temperature of the water being 19·0°C and the barometric pressure 769 mm. If the saturated vapour pressure of water at 19·0°C is 16·0 mm, calculate the gram equivalent weight of the metal.

The pressure of hydrogen to which the general gas equation (see 2.21) may be applied is $769-16 = 753$ mm.

N.B. Always subtract the saturated vapour pressure before applying the gas equation.

$$\text{Volume of hydrogen at N.T.P.} = \frac{753}{760} \times \frac{273}{292} \times 156\ \text{cm}^3 = \text{X cm}^3$$

By the gram molecular volume (2.20),
22400 cm^3 of hydrogen at N.T.P. weigh 2 g

$$\therefore \text{X cm}^3 \text{ of hydrogen at N.T.P. weigh } \frac{2}{22400} \times \text{X g}$$

This weight of hydrogen was displaced by 0·160 g of metal, i.e. 1 g of hydrogen would have been displaced by

$$0{\cdot}160 \times \frac{22400}{2} \times \frac{760}{753} \times \frac{292}{273} \times \frac{1}{156}\ \text{g} = 12{\cdot}4\ \text{g}$$

i.e. the gram equivalent weight of metal = 12·4 (magnesium)

(b) By direct combination with oxygen

(i) Where the oxide is a solid, e.g. MgO.

Weigh a crucible and lid. Insert a small coil of magnesium ribbon (cleaned with emery paper) and reweigh. Heat strongly, occasionally raising the lid. Allow to cool, add a few drops of water (to convert any Mg_3N_2 to MgO), and reheat. Allow to cool and reweigh. Repeat until the weight is constant, showing that reaction is complete.

(ii) Where the oxide is gaseous, e.g. carbon, sulphur.

Heat a weighed quantity of the element in a stream of air or oxygen. Collect the oxide by absorption in weighed bulbs of potassium hydroxide solution and hence find the increase in weight, due to absorption of the oxide.

The following (over-simplified) result may be obtained:

10 g of element → 14 g of oxide
∴ 10 g of element combine with 4 g of oxygen
∴ 20 g of element combine with 8 g of oxygen
∴ the gram equivalent weight = 20 g

(c) Conversion of metal to oxide with concentrated nitric acid

Example. Weigh a small quantity of zinc or tin in a weighed boiling tube and slowly add the minimum quantity of concentrated nitric acid needed to react completely with all the metal. Evaporate the solution slowly to dryness, shaking the tube continuously to prevent bumping or spitting. Heat strongly near the end of the heating, allow to cool, and weigh the test tube now containing the oxide.

Calculation—as above.

(d) Reduction of a metallic oxide

Reduce a known weight of the oxide (low in the electrochemical series, e.g. CuO, PbO) in a stream of hydrogen or coal gas (see section 6.5) and weigh the metal obtained. The change requires heat and it is important to continue passing coal gas or hydrogen while the metal is cooling (why?).

The calculation is similar to that in (*b*).

(e) Displacement of one metal by another

Example. Weigh a coil of thin iron wire or a piece of zinc foil. Place it in a basin and stir it with excess warm cupric sulphate solution; leave for as long as possible. Remove the copper produced (all the iron is now 'dissolved'), wash with distilled water, dry and weigh.

If it is found, say, that 1·03 g of zinc gave 1·00 g of copper, it follows that 32·5 g of zinc will replace 31·5 g of copper (the equivalent weight). Hence, the gram equivalent weight of zinc is 32·5 g.

$$\mathrm{Zn + Cu^{++} \rightarrow Zn^{++} + Cu}\downarrow$$

(f) By electrolysis (see 3.2)

(g) By titrimetric analysis

Dissolve a known weight of metal (e.g. Mg, Al, Fe) in excess of a solution of an acid of known concentration. Titrate the unused acid with standard alkali solution.

Example. 1·04 g of a metal was found to react with 32·2 cm³ of N-sulphuric acid. Calculate the gram equivalent weight of the metal.

$$1000 \text{ cm}^3 \text{ of N acid were used by } \frac{1{\cdot}04 \times 1000}{32{\cdot}2} \text{ g of metal}$$

$$= 32{\cdot}2 \text{ g}$$

i.e. $\underline{\text{the gram equivalent weight} = 32{\cdot}2 \text{ g.}}$

(h) The conversion ratio method

The equivalent weights of various acid radicals are taken as the weights of these radicals combining with 1 part by weight of hydrogen, for example:

$$\underset{1\qquad 35{\cdot}5}{\mathrm{HCl}} \qquad\qquad \underset{1\quad 48}{\mathrm{H_2SO_4}} \qquad\qquad \underset{1\quad 62}{\mathrm{HNO_3}}$$

If a given weight of one compound is converted into a measured weight of another compound, these weights are in the ratio of the equivalents of the compounds as calculated from the equivalent weight of the metal and the acid radicals.

Example. A solution containing 2·20 g of lead nitrate gave 2·02 g of lead sulphate on precipitation with sulphuric acid. If the equivalents of the nitrate and sulphate radicals are 62 and 48 respectively, find the equivalent weight of lead.

$$\frac{2{\cdot}20}{2{\cdot}02} = \frac{x + 62}{x + 48} \text{ (x = equivalent weight of lead)}$$

$$\underline{\text{giving } x = 103{\cdot}5.}$$

15.3 RELATIONSHIP BETWEEN EQUIVALENT AND ATOMIC WEIGHT

Let the formula of an oxide be X_2O_n, and let the atomic weight of X be A; n is the valency of X.

Then the molecular weight of the compound is 2A + 16n. That is:

16n parts by weight of oxygen unite with 2A parts of X

$$\therefore \quad 8 \text{ parts by weight of oxygen unite with } \frac{2A}{16n} \times 8$$

$$= \frac{A}{n} \text{ parts of X}$$

But, by definition, this is the equivalent weight of X. That is:

$$E = \frac{A}{n}$$

$$\therefore \quad \underline{A = E \times n}$$

or $\underline{\text{Atomic wt} = \text{Equivalent wt.} \times \text{valency.}}$

15.4 DULONG AND PETIT'S METHOD FOR ATOMIC WEIGHTS

The law (1819) stated that, for most solid elements,

$$\text{Atomic wt} \times \text{Specific ht} = \text{a constant (approx. 6·4)}$$

Exceptions include beryllium, boron, carbon and silicon.

1. The specific heat is determined.
2. The accurate equivalent weight is determined.
3. $V \times E = A$, but $A \times s = 6{\cdot}4$

$$\therefore \quad V = A/E = 6{\cdot}4/s.E$$

(where E = equivalent weight, A = atomic weight, V = valency (must be a whole number), s = specific heat)

Then $V \times E = A$.

Example. Zinc: gram equivalent weight by displacement of hydrogen = 32·5 g.

$$\text{Specific heat} = 0{\cdot}092 \text{ cal/g}$$

$$\text{Valency} = \frac{6{\cdot}4}{0{\cdot}092 \times 32{\cdot}5} = 2$$

$$\text{Atomic weight} = 2 \times 32{\cdot}5 = \underline{65{\cdot}0}$$

15.5 CANNIZZARO'S METHOD FOR ATOMIC WEIGHTS (1858)

1. The vapour densities, and hence molecular weights (see 2.22), of a *large number* of volatile compounds of an element are found; the method cannot be used unless the element forms a large number of such compounds.
2. The compounds are analyzed in order to find out the weight of element in a given weight of each one.
3. The weight of element in one gram molecule (2.20) of each compound is computed.
4. The most probable atomic weight is the smallest value obtained.

Example: carbon, where the volatile compounds could be CO_2, CO, C_2H_2, C_2H_4, CH_4, $(C_2H_5)_2O$ (diethyl ether), C_6H_6 (benzene), $CHCl_3$ (chloroform), for example:

Compound	*V.D.*	*M.W.*	*1 gram molecule*	*Percentage by weight of carbon in compound*	*Weight of carbon in 1 gram molecule*
Methane	8	16	16 grams	75·0%	12 g
Ethane	15	30	30 grams	80·0%	24 g
Acetylene	13	26	26 grams	92·3%	24 g
Benzene	39	78	78 grams	92·3%	72 g
Propane	22	44	44 grams	81·8%	36 g
Carbon dioxide	22	44	44 grams	27·3%	12 g

The smallest value obtained would be approximately 12.

It is possible to use the value of the atomic weight so obtained to find a valency, and hence the accurate atomic weight via an equivalent.

15.6 ACCURATE ATOMIC WEIGHTS

These are usually determined from a quantitative analysis of a compound of known formula, and containing other elements whose atomic weights are accurately known.

Example. 2·859 g of pure $CaCO_3$ gave, on ignition, 1·602 g of CaO. Find the atomic weight of calcium. (C = 12, O = 16)

$$\begin{array}{ccccc} CaCO_3 & \rightarrow & CaO & + & CO_2\uparrow \\ x + 12 + 48 & & x + 16 & & \end{array}$$

(x = atomic weight of calcium)

Hence,
$$\frac{x + 60}{x + 16} = \frac{2{\cdot}859}{1{\cdot}602}$$

By cross multiplication,

$$2{\cdot}859x + 45{\cdot}74 = 1{\cdot}602x + 96{\cdot}12$$
$$\therefore\quad 1{\cdot}257x = 50{\cdot}38$$
$$\therefore\quad x = 40{\cdot}08$$

i.e. atomic weight of calcium = 40·08.

15.7 DETERMINATION OF MOLECULAR WEIGHTS OF GASES BY DIFFUSION

Graham's law of diffusion has been given in 2.23. When a gas under pressure is forced through a fine orifice into a region containing another gas, the process is called *effusion*. The rate of diffusion of a gas is proportional to its rate of effusion. Hence, the relative rates of effusion of two gases are inversely proportional to the square roots of their molecular weights.

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

If t_1 and t_2 are the times taken for a given definite volume, V, of each gas to effuse into the air, then

$$r_1 = \frac{V}{t_1},\ r_2 = \frac{V}{t_2},\qquad \therefore\quad \frac{r_1}{r_2} = \frac{\frac{V}{t_1}}{\frac{V}{t_2}} = \frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$$

These times of effusion are measured with an effusiometer (fig. 15.3).

Each gas is admitted in turn and the time taken for the water level (or mercury level if either gas is soluble in water) to rise from M_1 to M_2 noted.

Example. Time for air (t_1) = 265 secs; time for hydrogen (t_2) = 70 secs; find the density of air.

Effusiometer

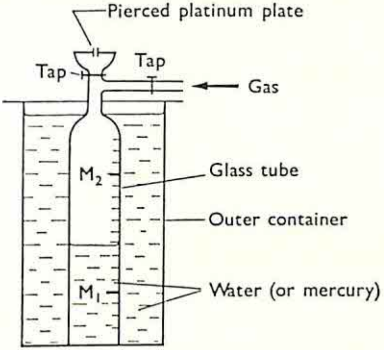


FIG. 15.3

From the theory developed,

$$\frac{265}{70} = \sqrt{\frac{D}{1}} \quad \text{(where D is the density of air)}$$

$$\therefore \quad D = \left(\frac{265}{70}\right)^2 = (3{\cdot}79)^2 = 14{\cdot}3(6)$$
$$= \underline{14{\cdot}4}$$

15.8 DETERMINATION OF MOLECULAR WEIGHTS OF GASES BY REGNAULT'S METHOD (MODIFICATION)

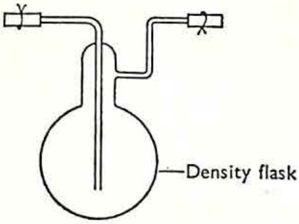


FIG. 15.4

The flask is weighed full of air at atmospheric pressure and temperature. It is then weighed full of gas (under test) at atmospheric pressure and temperature.

The volume of the flask is found by filling it with water.

Convenient gases are SO_2, CO_2, HCl. Care should be taken that the gas is passed through in the right direction (why?) and that the pressure is atmospheric when the clips are closed.

The volume is corrected to N.T.P. If it is assumed that 1 litre of air at N.T.P. weighs 1·29 g, the weight of air in the flask can be deduced. Hence, the weight of the 'empty' flask is determined, and therefore the weight of a known volume of the test gas at a definite temperature and pressure.

15.9 MOLECULAR WEIGHTS OF VOLATILE LIQUIDS

Several methods are available, and are discussed in more advanced textbooks. In Victor Meyer's method, a given weight of liquid is vaporized and this vapour displaces a corresponding volume of air which is collected in a graduated tube and measured under atmospheric conditions. Suitable liquids are chloroform, carbon tetrachloride, carbon disulphide, etc.

To calculate the vapour density (or molecular weight), we proceed as follows:

Let measured volume over water = V cm^3.

1. Correct to N.T.P., allowing for water vapour present = V_c cm^3
2. Then V_c cm^3 weigh ω g (i.e. the weight of liquid taken)

$$\therefore \quad 22{,}400\ \text{cm}^3 \text{ weigh } \frac{\omega}{V_c} \times 22{,}400 \equiv \underline{\text{M.W.}}$$

or

$$11{,}200\ \text{cm}^3 \text{ weigh } \frac{\omega}{V_c} \times 11{,}200 \equiv \underline{\text{V.D.}}$$

15.10 MOLECULAR FORMULAE OF GASES

(a) Volumes of gases reacting together

CARBON DIOXIDE, SULPHUR DIOXIDE

A small piece of graphite or sulphur is placed in the flask, which is filled with oxygen. Mercury in A is sucked up to a convenient level by means of a pump. The carbon or sulphur is heated, when it burns forming the dioxide. Initially, there is an expansion, since the gases are hot but, on cooling to the original conditions, it is found that there is no change in volume; therefore each gas contains its own volume of oxygen.

HYDROGEN SULPHIDE

A current of dry hydrogen sulphide is passed slowly through the tube and the ends of the tube are then sealed off in a blowpipe flame. The tube is warmed so that the metal combines with the hydrogen sulphide, forming the sulphide and leaving hydrogen. On cooling to room temperature, one end is broken under mercury. It is found that no

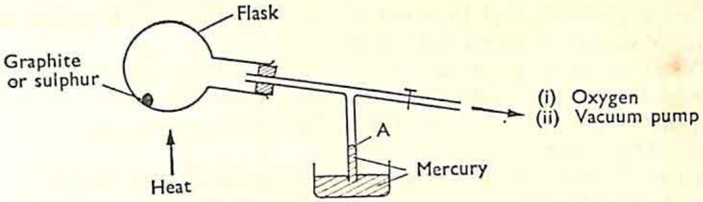


FIG. 15.5

mercury enters the tube, showing that there has been no change in volume.

HYDROGEN CHLORIDE

The two bulbs (of equal volume) are filled with hydrogen and chlorine respectively and the central tap is opened. After exposure to diffused light, and later to bright light, one end is opened under mercury. No mercury enters, showing that there is no decrease in volume.

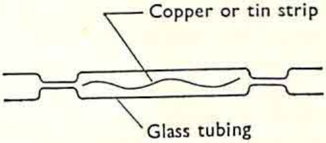


FIG. 15.6

The end is then closed, and later opened under a dilute aqueous solution of potassium iodide. Because of the ready solubility of hydrogen chloride (cf. fountain experiment) both bulbs are completely filled and the solution shows no brown colour due to iodine, which would be liberated if any free chlorine was present (13.3).

Hence hydrogen chloride only is left after the reaction, i.e. one volume of hydrogen plus one volume of chlorine react to give two volumes of hydrogen chloride.

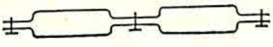


FIG. 15.7

AMMONIA

A glass tube is divided into three equal volumes by rubber bands and is filled with chlorine. A few cm^3 of 0·88 ammonia are dripped into the tube, which is kept cool by stroking it with a cloth soaked in ether.

The hydrogen in the ammonia combines with the chlorine forming hydrogen chloride, and then ammonium chloride, which settles as a white solid at the bottom of the tube.

Water containing a little dilute sulphuric acid (to dissolve any free ammonia) is dripped into the tube and fills two-thirds of its volume. This shows that the volume of residual gas (nitrogen) is one volume at atmospheric pressure.

This volume of nitrogen must have been combined with three volumes of hydrogen in ammonia, since it is known that three volumes of chlorine require three volumes of hydrogen to form hydrogen chloride.

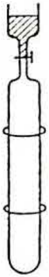


FIG. 15.8

Hence, there are three volumes of hydrogen to one volume of nitrogen.

WATER

Oxygen is passed into a eudiometer tube (fitted with a 3-way tap), and its volume is measured at atmospheric pressure. Hydrogen is then admitted and the additional volume measured, also at atmospheric pressure. The gases are sparked from an induction coil, with a cork in the right-hand side to prevent the escape of mercury.

The residual volume of gas is measured at atmospheric pressure. It is best to take about equal volumes of the two gases so that the remaining gas is oxygen. It is found that two volumes of hydrogen are united with one volume of oxygen, and that two volumes of steam are produced.

The experiment can be repeated for steam, the eudiometer tube being surrounded by a heating jacket of amyl alcohol vapour (b.p. 130°C). The additional final volume due to the fact that water remains as steam can be measured. It is again found that one volume of oxygen is united with two volumes of hydrogen.

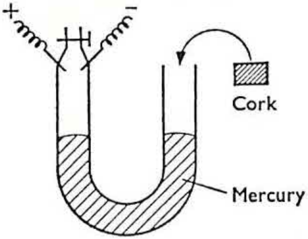


FIG. 15.9

N.B. Electrolysis of water containing a trace of an electrolyte (e.g. H_2SO_4) gives 2 volumes of hydrogen to every 1 volume of oxygen.

OXIDES OF NITROGEN

Iron wire ignited electrically in a closed volume of the gas combines with oxygen, leaving nitrogen.

1 volume of nitrous oxide → 1 volume of nitrogen

$$\therefore \quad N_2O \rightarrow N_2$$

2 volumes of nitric oxide → 1 volume of nitrogen

$$\therefore \quad 2NO \rightarrow N_2$$

With nitrogen dioxide, the result depends upon the percentage of N_2O_4 in the vapour.

(b) Molecular formulae

The general methods are

1. Gravimetric analysis plus a molecular weight determination.
2. Eudiometry plus a vapour density determination.

Example: Carbon dioxide

It is found that 1 volume of oxygen produces 1 volume of carbon dioxide. By Avogadro's hypothesis (see 2.1), 1 molecule of oxygen produces 1 molecule of carbon dioxide, i.e. the formula is C_xO_2. The experimentally determined vapour density (22) gives a molecular weight of 44.

Hence, $$12x + 32 = 44 \qquad \therefore \; x = 1$$
$$\therefore \; \underline{\text{formula is } CO_2}$$

The molecular formula of ozone

Two identical bulbs are filled with ozonized oxygen. In one case the ozone is absorbed by oil of turpentine while in the other it is heated to give oxygen. Results show that the contraction in volume when the ozone is absorbed to the volume of oxygen produced is 2 : 3

∴ 2 volumes of ozone → 3 volumes of oxygen

By Avogadro's hypothesis (see 2.1)

2 molecules of ozone → 3 molecules of oxygen (O_2)

that is $$\underline{\text{ozone is } O_3}$$

Formulae of gaseous hydrocarbons

A known volume of the compound is exploded with excess oxygen over mercury in a eudiometer tube. The volume of carbon dioxide produced is determined by absorption in potassium hydroxide solution while steam is usually condensed to water of negligible volume. Sometimes, excess oxygen is absorbed in alkaline pyrogallol.

If the formula is C_xH_y, the general reaction is:

$$C_xH_y + \left(x + \frac{y}{4}\right) \quad O_2 \rightarrow \ xCO_2 \ + \qquad \frac{y}{2}H_2O$$

$$1 \text{ vol} \quad \left(x + \frac{y}{4}\right) \text{vol} \quad \rightarrow \quad x \text{ vol} \qquad \text{negligible vol (if water)}$$

$$\text{Contraction on sparking} = \left(1 + \frac{y}{4}\right) \text{vol.}$$

$$\text{Contraction with potash} = x \text{ vol.}$$

Example. After 10 cm^3 of a gaseous hydrocarbon had been exploded with 60 cm^3 of oxygen, the volume of remaining gases was 45 cm^3. 20 cm^3 of this were absorbed with potash. Find the molecular formula of the hydrocarbon, assuming that all measurements were made at room temperature and pressure.

Let 10 cm^3 = 1 volume. Volume of $CO_2 = 20 \text{ cm}^3 = 2$ vol, i.e. $x = 2$

Contraction on sparking $= (10 + 60 - 45) = 25 \text{ cm}^3 = 2{\cdot}5$ vol

$$\therefore \quad 1 + \frac{y}{4} = 2{\cdot}5, \qquad \text{i.e. } y = 6$$

$\therefore$ molecular formula is C_2H_6 (ethane)

15.11 QUESTIONS

1. 0·60 g of a metal liberated from an acid 170 cm^3 of hydrogen at N.T.P. Find the equivalent weight of the metal. [39·2]

2. A metal has an equivalent weight of 12. What volume of hydrogen at N.T.P. would be evolved when 0·270 g of it reacts completely with an excess of a dilute acid? [250 cm^3]

3. If 10·2 g of a metallic oxide gave 8 g of the metal on reduction, find the equivalent weight of the metal. [29·1]

4. When 2·55 g of zinc were reacted with dilute nitric acid and the solution was evaporated and heated, 3·18 g of residue remained. What is the equivalent weight of zinc? [32·5]

5. 0·50 g of a mixture of zinc powder and aluminium gave, with dilute acid, 280 cm^3 of hydrogen. Find the percentage composition of the mixture by weight. [24·4% Al, 75·6% Zn]

6. Describe how the equivalent weight of magnesium might be determined by utilizing the displacement of hydrogen from a dilute acid.

7. Describe the determination of the equivalent weight of copper by reduction of its oxide.

8. 0·385 g of iron liberated, from hydrochloric acid, 169 cm^3 of hydrogen measured over water at 20°C and 755 mm. The S.V.P. of water at 20°C is 18 mm. Find the equivalent weight of iron. [28·0]

9. An element M has a valency of 2. It is found that 1·4 g of M displace all the hydrogen from 2·45 g of sulphuric acid. Find the equivalent and atomic weight of X. [28, 56]

10. The equivalent weight of zinc is 32·5. 65 g of zinc precipitate 64 g of copper when added to excess of cupric sulphate solution. Find the equivalent of copper. [32]

11. 1·656 g of lead are dissolved in nitric acid and precipitated as lead sulphate by dilute sulphuric acid. The weight of lead sulphate is 2·424 g. Find the equivalent weight of lead, given that the equivalent of the sulphate radical is 48. [103·5]

12. A metal X forms two chlorides (anhydrous). From 2·00 g of the metal, 4·54 g and 5·80 g of the chlorides can be produced, respectively. Find the equivalent weights of the metal. The equivalent of chlorine is 35·50. [27·95, 18·68]

13. Explain carefully how Dulong and Petit's law can be used to determine atomic weights, pointing out its limitations.

14. The specific heat of an element is 0·032 cal/g. Find its approximate atomic weight. If the equivalent weight of this element in one of its compounds is 65·57, find the accurate atomic weight. [196·7]

15. The specific heat of a metal is 0·056. When 0·75 g of the metal was reacted with excess of a dilute acid, 158 cm^3 of dry hydrogen at 15°C and 750 mm were evolved; find the atomic weight of the metal. [112·76]

16. Derive the relationship between equivalent weight, valency and atomic weight.

17. Define (*a*) valency, (*b*) equivalent weight of an element. The formula of an oxide of a metal X is X_2O_3. If the oxide contains 80 per cent of X, (*a*) find the valency of X, (*b*) find the equivalent weight of X, (*c*) find the atomic weight of X.

18. When a current of 0·5 amp was passed through a solution of an electrolyte for 32 min 10 sec, 0·406 g of a metal X was deposited. The vapour density of the anhydrous chloride of the metal was 114. Find the probable atomic weight of X. 1 faraday = 96,500 coulombs. [121·8]

19. Describe carefully the determination of the molecular formula of ammonia.

20. Describe the determination of the molecular formula of sulphur dioxide.

21. A mixture of oxygen and hydrogen occupies 24·4 cm³. After sparking, the gas remaining (oxygen) occupies 3·7 cm³. Find the composition of the mixture. [13·8 cm³ H_2, 10·6 cm³ O_2]

22. A metal X has a valency of 3 and its sulphate has 18 molecules of water of crystallization. 10 g of the crystalline sulphate gave 1·530 g of the oxide. Find the atomic weight of X. [26·95]

23. A strip of a metal M, weighing 2·25 g was converted to the oxide (3·34 g). The atomic weight of the metal was 45; what is the valency. What weight of the chloride would be produced if 2 g of M were heated in a stream of dry chlorine? [3, 6·73 g]

24. The chloride of a divalent metal contains 64 per cent chlorine. Find the atomic weight of the metal. [39·9]

25. A metal M forms two oxides. 24·0 g of the first oxide contain 4·8 g of oxygen; 16·0 g of the second oxide contain 4·0 g of oxygen. Find the probable atomic weight of M. [96]

26. 0·56 g of a metal M liberated 224 cm³ of hydrogen at N.T.P. from excess dilute hydrochloric acid. Calculate the equivalent weight of M. If an oxide of M contained 30 per cent of oxygen by weight, what is the probable atomic weight of M? [28, 56]

16 Rate of Reaction and the Law of Mass Action

16.1 THE LAW OF MASS ACTION (GULDBERG AND WAAGE, 1867)

STATE INSTITUTE OF EDUCATION * Govt. of West Bengal *

The velocity of a chemical change is directly proportional to the 'active masses' of the reacting substances.

'Active mass' is the concentration in g-molecules per litre (gases, substances in solution), or pressures (gases). The active mass of a solid is a constant.

That the rate of reaction is greater the greater the concentration of a given reactant can be seen from the following experiment. If 5 cm³ portions of 0·2 molar (0·2 normal) hydrochloric acid are added to separate 5 cm³ portions of 1·5 molar (1·5 normal), 1 molar (1 normal) and 0·25 molar (0·25 normal) solutions of sodium thiosulphate, and the times when the sulphur first appears (milkiness) are recorded, it will be found that the reciprocal of the times is proportional to the original concentration of sodium thiosulphate, i.e.

$$\text{Rate of reaction} \propto \frac{1}{\text{Time}} \propto \text{Concentration of thiosulphate}$$

In this experiment a constant concentration of acid is used.

By mixing the same thiosulphate and acid solutions at different temperatures (say 30°C, 60°C), it can easily be shown that rise of temperature causes an increased rate of reaction.

$$S_2O_3^{--} + 2H^+ \rightarrow SO_2 + H_2O + S$$

Chemical reactions can be classified as either irreversible, which proceed completely in one direction, or reversible, in which the forward and reverse reactions both proceed appreciably and eventually reach a state of *chemical equilibrium* (here the rate at which molecules of reactants pass into products balances the rate at which molecules of products decompose). In general, ionic reactions are irreversible and instantaneous, for example:

$$Na^+ + OH^- + H^+ + Cl^- \rightarrow Na^+ + Cl^- + H_2O$$
$$Ag^+ + NO_3^- + H^+ + Cl^- \rightarrow AgCl\downarrow + H^+ + NO_3^-$$

It is important to realize, however, that a reversible reaction can be 'complete' under each set of conditions. Thus the reaction

$$2Sb^{3+} + 3H_2S \rightleftharpoons Sb_2S_3 + 6H^+$$

is a reversible reaction hardly ever regarded as an equilibrium. The reaction

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$

is reversible, but does not set up an equilibrium under the conditions used in the preparation of hydrogen.

16.2 THE EQUILIBRIUM CONSTANT

Using the law of mass action, it is possible to deduce, for a reversible reaction, an important quantity called the equilibrium constant.

Consider a general reversible reaction.

$$A + B \rightleftharpoons C + D$$

By the law of mass action, the velocity of the forward reaction is given by:

$$v_1 = k_1[A][B]$$

The velocity of the reverse reaction is given by:

$$v_2 = k_2[C][D]$$

When equilibrium is reached, $v_1 = v_2$

$$\therefore \quad k_1[A][B] = k_2[C][D]$$

$$\therefore \quad k_1/k_2 = K = \frac{[C][D]}{[A][B]}$$

where k_1, k_2 are called velocity (rate) constants, K is the equilibrium constant, and the square brackets represent 'active masses'. By convention, the equilibrium constant is written as the product of the concentrations of the substances produced in the forward reaction divided by the product of the concentrations of the reactants in the forward reaction.

It can be shown that the same expression for K holds whatever the mechanism of the reaction.

If, then, the concentration of reactant A in a particular reversible reaction involving A, B, C, D is raised, *and B is kept constant*, the result is a decrease in the concentration of B and an increase in the concentrations of C and D. Consider the reaction of steam on red-hot iron.

$$\overset{A}{3Fe} + \overset{B}{4H_2O} \rightleftharpoons \overset{C}{Fe_3O_4} + \overset{D}{4H_2}$$

(*a*) If the active mass of steam is increased, *and the active mass of a solid is constant*, hydrogen is produced.

(*b*) If the active mass of hydrogen is increased, *and the active mass of a solid is constant*, steam is produced.

(*c*) The reaction depends only upon the partial pressures of two gases because two solids are concerned.

In the dissociation of calcium carbonate,

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

if the carbonate is heated in an open vessel so that the carbon dioxide can escape, the reaction proceeds completely to the right; if, however, the carbonate is heated in a closed vessel to which carbon dioxide is added under slight pressure, the reaction proceeds to the left.

Note again that the reaction involves two solids and therefore depends only on the partial pressure of carbon dioxide.

In the Haber process,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad \Delta H = -24 \text{ kilocalories (evolved)}$$

an excess of hydrogen must be used for a given concentration of nitrogen if there is to be a large quantity of ammonia at equilibrium.

Le Chatelier's principle (see 8.8) is a useful rule which predicts qualitatively what the expression for the equilibrium constant can do quantitatively.

Le Chatelier's principle is of great value in predicting the effect of temperature and pressure on the equilibrium mixture of a reversible reaction, as has already been explained for the Haber (9.4) and Contact (8.8) processes.

(*a*) Exothermic reactions—favoured by low temperatures.

(*b*) Endothermic reactions—favoured by high temperatures.

(*c*) Gaseous reactions in which there is a decrease in the number of molecules in the forward direction—forward products favoured by high pressures.

(*d*) Gaseous reactions in which there is an increase in the number of molecules in the forward direction—favoured by low pressures.

(*e*) Gaseous reactions in which there is no change in the number of molecules—pressure has no effect on the equilibrium mixture (but it does affect the rate).

Examples

(*a*) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ heat liberated = 24 kilocal.
$2SO_2 + O_2 \rightleftharpoons 2SO_3$ heat liberated = 45 kilocal.

(*b*) $N_2 + O_2 \rightleftharpoons 2NO$ heat absorbed = 43 kilocal.

$C + H_2O \rightleftharpoons \underset{\text{water gas}}{\overbrace{CO + H_2}}$ heat absorbed = 32 kilocal.

(*c*) $N_2 + 3H_2 \rightleftharpoons 2NH_3$
(4 mol → 2 mol)
$2SO_2 + O_2 \rightleftharpoons 2SO_3$
(3 mol → 2 mol)

(*d*) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
(1 mol → 2 mol)

(*e*) $2HI \rightleftharpoons H_2 + I_2$
(2 mol → 2 mol)
$N_2 + O_2 \rightleftharpoons 2NO$
(2 mol → 2 mol)

16.3 FACTORS INFLUENCING REACTION

The law of mass action shows quantitatively how the velocity of a chemical reaction depends upon the initial concentrations of the reactants.* The rate is measured by the number of gram-molecules of a reactant undergoing reaction in unit time. In a more advanced text, you will learn about this quantitative treatment (order and molecularity of a reaction). The *molecularity* of a reaction is merely the number of molecules reacting according to the 'rate-determining' step of the reaction. Most reactions can be broken down into several stages, which take place at different rates, the slowest stage being 'rate-determining'. The *order* is the number of atoms or molecules whose concentrations determine the rate of reaction.

Suppose that A and B react to give products, and that

$$\text{Rate of reaction} = k[A]^m[B]^n$$

where k is the rate constant, the square brackets represent concentrations in gram-molecules per litre, and m and n are numbers (0, 1, 2 or occasionally fractions). The sum (m + n) for a reaction is the order of reaction. The order is m with respect to A and n with respect to B.

We find that the rate of a reaction (or the rate of establishment of equilibrium of a reversible reaction) is increased by having a greater concentration of any one (or all) reactant(s). This can be deduced from the kinetic theory by assuming that the velocity of a reaction is proportional to the number of molecular collisions per second.

The rate of a reaction is always increased by employing a higher temperature. This is expected, since the velocity of all reacting molecules is increased by heating, this giving rise to a greater number of molecular collisions per second. A 10°C rise in temperature approximately doubles the rate of reaction. For gaseous reactions, an increase of pressure brings the reacting molecules closer together, increasing the concentration, and therefore increasing the rate of molecular collisions (i.e. the rate of reaction increases). Since pressure has a negligible effect on the volume of a solid or liquid, it affects only gaseous reactions.

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* As you will see at a later stage in your chemistry studies, however, many reactions do not follow the simple law of mass action.

The effect of pressure and temperature changes on reversible reactions has already been mentioned.

The rate of a reaction is frequently affected by the physical states of the reactants, and by the presence of substances called catalysts (see 16.4).

The reaction between sodium thiosulphate solution and dilute hydrochloric acid, given in 16.1, can be used to show the way in which concentration influences the rate of a reaction. The effect of temperature on the rate of a reaction can also be studied by carrying out the reaction at two different temperatures.

Alternatively, the reaction between marble and hydrochloric acid can be studied.

$$CO_3^{--} + 2H^+ \rightarrow CO_2\uparrow + H_2O$$

The marble is placed on a balance and the weight determined at regular intervals.

16.4 CATALYSIS

A catalyst is a substance which increases the rate of a chemical reaction without being itself affected in quantity or in chemical composition. Some substances decrease the rate of a reaction and are sometimes called 'negative catalysts'.

In a given reaction, several different catalysts may be effective, but they will differ in efficiency; many industrial processes depend for success on the choice of the most efficient catalyst.

There are some cases where the nature of the final products may depend on the catalyst.

It should be clearly understood that the position of equilibrium of a reversible reaction is unaffected by the presence of a catalyst. The forward and reverse reactions are speeded up equally, i.e. only the rate of attainment of equilibrium is altered.

The importance of catalysts depends upon their effect on reversible exothermic reactions where the alternative method for increasing the rate (i.e. raising the temperature) would produce a diminished yield.

Although a catalyst is unchanged chemically at the end of a reaction, its physical state may be altered, e.g. if granular manganese dioxide is used to catalyse the decomposition of potassium chlorate by heat, it is obtained as a fine powder at the end of the reaction.

A catalyst is usually specific, i.e. a catalyst for one reaction will not usually be suitable for another reaction. On the other hand, some substances (e.g. platinum) will catalyse a wide variety of reactions.

A minute trace of catalyst will often continue to work indefinitely. A catalyst only alters the rate of reaction and not the yield of product.

The efficiency of a catalyst is often changed by the presence of another substance. If the efficiency is *increased*, the substance is called a *promoter*. If the efficiency is *decreased*, it is called an *inhibitor* or *poison*. Thus, alumina promotes the ferric oxide catalyst in the Haber process. Catalyst prisons are usually those which poison the body, e.g. hydrogen cyanide, hydrogen sulphide, arsenious oxide.

Enzymes are biochemical catalysts, and can affect many important reactions, e.g. glucose is converted to ethanol by zymase in yeast.

In *autocatalysis*, the reaction is catalysed by one of the products, e.g. the rate of oxidation of oxalic acid by acidified potassium permanganate is catalysed by manganous ions produced.

$$2MnO_4^- + 6H^+ + 5(COOH)_2 \rightarrow 2Mn^{++} + 8H_2O + 10CO_2\uparrow$$

The change from white tin to grey tin is catalysed by grey tin—this is one of the reasons for the failure of Scott's expedition to the Pole, since his fuel cans decomposed owing to the autocatalysis of white to grey tin by spots of grey tin (produced at the very low Polar temperature).

Some reactions are catalysed by light, this being called *photocatalysis*, e.g. photosynthesis reaction, reaction of hydrogen with chlorine.

Examples of catalysis

1. The Haber process for ammonia (ferric oxide, promoted by alumina).
2. The Contact process for sulphuric acid (vanadium pentoxide).
3. The decomposition of potassium chlorate to prepare oxygen (MnO_2, CuO, FeO, or NiO).
4. The Chamber process for sulphuric acid (nitric oxide).
5. The catalytic hydrogenation reactions, e.g. oils to fats (finely-divided nickel).
6. The water-gas reaction (nickel).
7. The decomposition of hypochlorites (cobaltous ions).

When the catalyst and reactants are in the same physical state (really, the same *phase*), the catalysis is said to be *homogeneous*. When they are in different physical states (phases), the catalysis is said to be *heterogeneous*.

Both homogeneous and heterogeneous catalysis are thought to proceed via the formation of an *intermediate* chemical 'compound', although this cannot generally be assigned a true formula in heterogeneous catalysis. The mechanism of catalysis is best left to a more advanced textbook.

16.5 QUESTIONS

1. State the law of mass action. Explain what will happen when concentrated hydrochloric acid (concentration >50 per cent by weight) is added to the following equilibrium system:

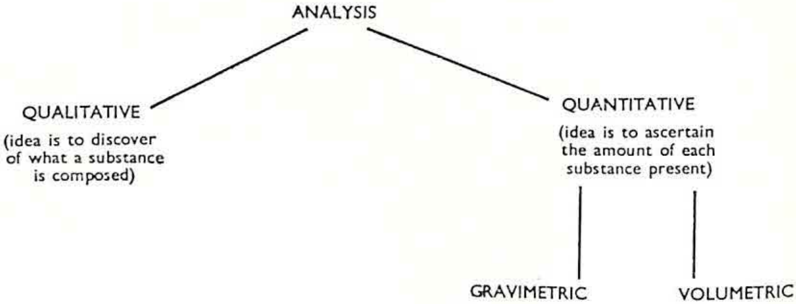
$$BiCl_3 + H_2O \rightleftharpoons BiOCl\downarrow + 2HCl$$

2. Account for the conditions under which (*a*) the Haber process, (*b*) the Contact process are carried out.
3. Give an account of the factors influencing chemical reaction.
4. What is a catalyst? State three characteristics of a catalyst. Name two reactions in which a catalyst is used (*a*) in the laboratory, (*b*) in industry.
5. Write briefly on (*a*) velocity constants, (*b*) equilibrium constants, (*c*) catalysts. How does a catalyst affect a reversible reaction?
6. Describe simple experiments you would yourself perform in order to show that the reactions
   (*a*) $NH_4Cl \rightleftharpoons NH_3 + HCl$
   (*b*) $3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$
   are reversible, stating the test you would carry out to prove your statements.
7. Describe how you would show that an increase of temperature increases the rate of formation of sulphur when sodium thiosulphate solution is acidified with hydrochloric acid.

17 Quantitative Analysis

17.1 INTRODUCTION

Synthesis—building up of a substance from simpler substances.
Analysis—breaking down of a substance in order to discover something about its constituents.


ANALYSIS
QUALITATIVE
(idea is to discover of what a substance is composed)
QUANTITATIVE
(idea is to ascertain the amount of each substance present)
GRAVIMETRIC
VOLUMETRIC

17.2 GRAVIMETRIC ANALYSIS

This involves *very accurate* weighing. For example, the percentage of silver in a silver/copper alloy is determined by dissolving the alloy in concentrated nitric acid (converting both metals to nitrates) followed by precipitation of silver chloride with hydrochloric acid. The precipitate is filtered off, washed, dried and weighed. Since silver chloride contains $\frac{107\cdot9}{143\cdot5} \times 100$ per cent ($=75\cdot4$ per cent) of silver, it follows that the weight of alloy which gives 100 g of silver chloride contains 75·4 g of silver.

Sulphate ion concentration can be estimated as barium sulphate.

$$\begin{aligned} \mathrm{Ba^{++}} + \mathrm{SO_4^{--}} &\rightarrow \mathrm{BaSO_4}\downarrow \\ 96\ \mathrm{g} &\rightarrow 233\ \mathrm{g} \end{aligned}$$

The gravimetric composition of water is discussed in 7.11.

The percentage of water of crystallization in a hydrated salt can be determined by measurement of its percentage loss in weight on heating (the anhydrous salt is formed), for example:

$$BaCl_2.xH_2O \xrightarrow{\text{heat}} BaCl_2 + xH_2O\uparrow$$

$$\text{per cent loss in weight} = \frac{\text{loss in weight}}{\text{weight taken}} \times 100$$

$$\text{Theoretical loss in weight} = \frac{18x}{18x + 208} \times 100$$

(where 208 is the formula weight of $BaCl_2$ and 18 is the molecular weight of H_2O).

In a typical determination, per cent loss in weight = $14{\cdot}75$

$$\therefore \quad \frac{18x}{18x + 208} \times 100 = 14{\cdot}75$$

$$\underline{\text{giving } x = 2}$$

Solubility can be determined by gravimetric analysis of a saturated solution (see 14.2).

17.3 TITRIMETRIC OR VOLUMETRIC ANALYSIS

This is *less accurate* than gravimetric analysis but *more rapid. Weights* of substances in solution are determined by measurement of *volumes* of solution.

A *standard solution* is one of known concentration (usually expressed as grams per litre). Sometimes the concentration is quoted as a percentage, e.g. a 10 per cent solution contains 10 g of solute per $(100 - 10) = 90$ g of solvent.

A *molar solution* contains 1 gram-molecule (or 1 gram-formula weight) of solute per litre of solution.

Equivalent weights of compounds

1. The equivalent weight of an acid is the number of parts by weight of it which *produces one* part by weight of hydrogen in the form of a proton, for example:

$$\underset{1\quad 35{\cdot}5}{\underset{/\quad\backslash}{HCl}} \equiv H^+ \qquad \underset{2\quad 32\quad 64}{\underset{/\quad|\quad\backslash}{H_2SO_4}} \equiv 2H^+ \qquad \underset{3\quad 31\quad 64}{\underset{/\quad|\quad\backslash}{H_3PO_4}} \equiv 3H^+$$

$$\therefore \quad \text{E. Wt} = \underline{36{\cdot}5} \quad \therefore \quad \text{E. Wt} = \frac{98}{2} = \underline{49} \quad \therefore \quad \text{E. Wt} = \frac{98}{3} = \underline{32{\cdot}67}$$

$$\text{Equivalent weight} = \frac{\text{Formula weight}}{\text{basicity}}$$

where *basicity* is the number of protons produced per 'molecule' of acid.

2. The equivalent weight of a base is the number of parts by weight of it which reacts with or accepts *one* part by weight of hydrogen in the form of a proton.

(*a*) $OH^- + H^+ \rightarrow H_2O$

$$\begin{aligned} \therefore \quad \text{E. Wt of } OH^- &= \text{formula weight} \\ \therefore \quad \text{E. Wt of } Na^+OH^- &= \text{formula weight} \\ &= \underline{40} \end{aligned}$$

(*b*) $CO_3^{--} + 2H^+ \rightarrow H_2CO_3$

$$\begin{aligned} &\therefore \quad \text{E. Wt of } CO_3^{--} = \tfrac{1}{2} \text{ formula weight} \\ &\therefore \quad \text{E. Wt of } (Na^+)_2CO_3^{--} \quad \text{or} \\ &(Na^+)_2CO_3^{--}.10H_2O = \tfrac{1}{2} \text{ formula weight} \\ &\qquad = \frac{106}{2} \quad \text{or} \quad = \frac{106 + 180}{2} \\ &\qquad = \underline{53} \qquad\qquad = \underline{143} \end{aligned}$$

(*c*) $O^{--} + 2H^+ \rightarrow H_2O$

$$\begin{aligned} \therefore \quad \text{E. Wt of } O^{--} &= \tfrac{1}{2} \text{ formula weight} \\ \therefore \quad \text{E. Wt of CuO} &= \tfrac{1}{2} \text{ formula weight} \\ &= \tfrac{1}{2} \times 79{\cdot}5 = \underline{39{\cdot}75} \end{aligned}$$

(*d*) $Mg + 2H^+ \rightarrow Mg^{++} + H_2$

$$\begin{aligned} \therefore \quad \text{E. Wt of Mg} &= \tfrac{1}{2} \text{ atomic weight} \\ &= \tfrac{1}{2} \times 24{\cdot}5 = \underline{12{\cdot}25} \end{aligned}$$

3. The equivalent weight of an oxidizing agent is the number of parts by weight of it requiring 1 electron for reduction, for example:

(*a*) $MnO_4^- + 8H^+ + 5e \rightarrow Mn^{++} + 4H_2O$

$$\text{E. Wt of } KMnO_4 = \frac{\text{Formula Wt}}{5}$$

(*b*) $Cr_2O_7^{--} + 14H^+ + 6e \rightarrow 2Cr^{+++} + 7H_2O$

$$\text{E. Wt of } K_2Cr_2O_7 = \frac{\text{Formula Wt}}{6}$$

The equivalent weight of a reducing agent is the number of parts by weight of it which provides 1 electron for reduction, for example:

(*a*) $Fe^{++} \rightarrow Fe^{+++} + 1e$

E. Wt of $FeSO_4$ = Formula Wt

(*b*) $(COOH)_2 \rightarrow 2CO_2 + 2H^+ + 2e$

$$\text{E. Wt of } (COOH)_2 = \frac{\text{Formula Wt}}{2}$$

(*c*) $2S_2O_3^{--} \rightarrow S_4O_6^{--} + 2e$

E. Wt of $Na_2S_2O_3$ = Formula Wt

A *normal solution* contains 1 gram-equivalent of the substance in 1 litre of solution.

$$\text{1 litre of 1N-acid reacts with} \begin{cases} \text{1 litre of 1N-alkali} \\ \text{1 litre of 1N-carbonate (soluble)} \\ \text{1 litre of 1N-bicarbonate} \\ \text{1 g-equiv. of any base or metal} \end{cases}$$

N.B. (*a*) Solution 1 reacted with Solution 2

$N_1 \times V_1 = N_2 \times V_2$
(N = normality, V = volume)

(*b*) $$\text{Normality} = \frac{\text{Grams per litre}}{\text{Equivalent weight}}$$

Also (*c*) $M_1 \times V_1 = M_2 \times V_2$ (M = molarity) provided 1 formula-weight of compound 1 reacts with 1 formula-weight of compound 2. For, say

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$$

two formula-weights of alkali are equivalent to one formula-weight of acid: equating number of formula-weights reacting we get:

$$\begin{array}{ccc} \textit{Alkali} & & \textit{Acid} \\ \dfrac{M_1 \times V_1}{1000} & : & \dfrac{M_2 \times V_2}{1000} \\ 2 & : & 1 \end{array}$$

and so $\underline{M_1 \times V_1 = 2 \times M_2 \times V_2}$

(*d*) $$\text{Molarity} = \frac{\text{Grams per litre}}{\text{Formula weight}}$$

Titrations

The concentration of a solution of a substance can be determined if a standard solution of another substance, which will react with it quantitatively, is provided and if a suitable indicator (see 6.7) is available to show the 'end point' of the reaction.

In acidimetry/alkalimetry, the indicator is usually one of the three common ones mentioned in 6.7. The choice of indicator depends upon the acid and alkali to be titrated. This can be deduced, but it will be left to a more advanced textbook.

Strong acid versus strong alkali—use methyl orange, litmus or phenolphthalein
Weak acid (that is, organic acids) versus strong alkali—use phenolphthalein (or litmus)
Weak alkali versus strong acid—use methyl orange (or litmus)
Weak acid versus weak alkali—no satisfactory end point can be obtained using any indicator

In many redox titrations, e.g. those involving potassium permanganate, no indicator is needed since the permanganate solution is its own indicator because it is so highly coloured. Thus, if potassium permanganate solution is reacted with a solution containing ferrous ions, the end point is when the latter solution changes from pale green to purple (excess permanganate).

Titration is carried out using a pipette and burette (fig. 17.1).

Titrimetry

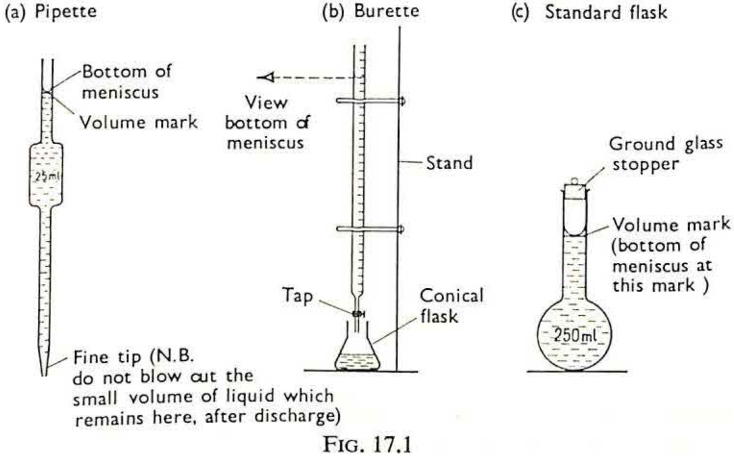


FIG. 17.1

In order to make up a standard solution, a known weight of the solid is dissolved in a small volume of the solvent (e.g. deionized water) and the solution is then made to a definite volume (e.g. 250 cm^3) in a standard flask using the same solvent. Suitable substances for making standard solutions must be pure, non-hygroscopic, non-efflorescent, non-deliquescent, and reasonably soluble in water.

Examples

1. How must 1·2 N hydrochloric acid be diluted in order to make N solution? 1000 cm^3 of 1·2 N hydrochloric acid are equivalent to 1200 cm^3 of N solution, since the 1·2 N solution is $\frac{1200}{1000} = 1{\cdot}2$ N. Hence, if 1000 cm^3 is made up to 1200 cm^3 with deionized water, it will become N. Hence, 200 cm^3 of water must be added to every 1000 cm^3 of 1·2 N solution, and so on in proportion.

2. A 0·1 N solution of hydrochloric acid was titrated with sodium hydroxide solution of unknown concentration. 25 cm^3 of the alkali were exactly neutralized by 20·2 cm^3 of the acid. Find the normality of the alkali and the concentration in g/l.

$$\underset{\text{Alkali}}{N_1 \times V_1} = \underset{\text{Acid}}{N_2 \times V_2}$$

$$x \times 25 = 0{\cdot}1 \times 20{\cdot}2$$

$$x = \frac{0{\cdot}1 \times 20{\cdot}2}{25} = 0{\cdot}0808\ \text{N}$$

Equivalent weight of NaOH = 40

$$\text{Normality} = \frac{\text{g/l}}{\text{E. Wt}}$$

$$\therefore\quad \text{Concentration} = 0{\cdot}0808 \times 40 = \underline{3{\cdot}232\ \text{g/l}}$$

The concentration can be obtained without use of normalities, and there is a tendency nowadays to use this method.

$$\underset{\text{1 equiv.}}{\overbrace{H^+ + Cl^-}} + \underset{\text{1 equiv.}}{\overbrace{Na^+ + OH^-}} \rightarrow \overbrace{Na^+ + Cl^-} + H_2O$$

20·2 cm^3 of 0·1 N HCl contains $\frac{20{\cdot}2}{1000} \times 0{\cdot}1$ g-equiv. of HCl, and this must be equivalent to the same number of g-equiv. of NaOH (see equation). Hence, this is the number of g-equiv. of NaOH in 25 cm^3

of solution, giving the number per litre as $\frac{20{\cdot}2}{1000} \times 0{\cdot}1 \times \frac{1000}{25}$. The number of grams per litre is therefore

$$\frac{20{\cdot}2}{1000} \times 0{\cdot}1 \times \frac{1000}{25} \times 40 = \underline{3{\cdot}232 \text{ g/l}}$$

N.B. 1. To estimate the number of molecules of water of crystallization in sodium carbonate (hydrated), a definite weight of the crystals is dissolved in deionized water in a beaker and then made up to volume in a standard flask. 25 cm^3 portions are titrated with standard hydrochloric acid using methyl orange and, from the results, the normality of the carbonate solution is determined. The concentration of *anhydrous* sodium carbonate can thus be determined (in g/250 cm^3). Since the weight of hydrated compound is known, it is possible to calculate how much water of crystallization this weight of hydrated salt must have contained. This value is expressed as a percentage, and the number of molecules of water of crystallization determined from the formula:

$$\text{per cent water of crystallization} = \frac{18x}{106 + 18x} \times 100$$

2. To estimate the amount of ammonia in a given specimen of an ammonium salt, ammonia is expelled from the salt by boiling it with sodium hydroxide solution (known excess) and that remaining is then estimated by titration with a standard acid. Hence, the volume of alkali which has reacted with the given quantity of ammonium salt can be deduced.

3. To determine the equivalent weight of a metal, proceed as in 15.2.

Experimental technique

You will learn this only by constant practice. Read the burette to 0·1 cm^3 accuracy (0·05 cm^3 if possible). Take one approximate reading and AT LEAST two accurate ones. Take the average of the accurate readings. Add solution DROP BY DROP near the endpoint.

17.4 QUESTIONS

1. What weight of anhydrous sodium carbonate is required to make 250 cm^3 of N/2 solution? [6·625 g]
2. What volumes of N H_2SO_4 are needed to neutralize (*a*) 20 cm^3 of 1·25 N Na_2CO_3, (*b*) 10 cm^3 of N KOH?

3. 25 cm^3 of a solution of sodium carbonate containing 5·3 g/l (anhydrous salt) were neutralized by 20 cm^3 of sulphuric acid. Find the concentration of the acid in g/l. [6·125]

4. 25 cm^3 of 0·1 N potassium hydroxide solution was added to 50 cm^3 of 0·12 N hydrochloric acid and the mixture made to 250 cm^3 with deionized water. What volume of 0·05 N potassium hydroxide solution would just neutralize 25 cm^3 samples of the solution? [7 cm^3]

5. 1 litre of dry hydrogen chloride at 15°C and 740 mm was dissolved in water. What volume of potassium hydroxide solution containing 56 g/l would be required to neutralize the acid? [41·21 cm^3]

6. 11·2 litres of dry ammonia at N.T.P. were dissolved in water. What volume of 2 N hydrochloric acid would be required to neutralize the alkali? [250 cm^3]

7. What volume of dry ammonia at 17°C and 770 mm would be required to give 1 litre of 0·1 N ammonia solution? If this volume of solution is reacted with sulphuric acid, what weight of ammonium sulphate is formed? [2348 cm^3, 6·92 g]

8. 25 cm^3 of a solution of sodium carbonate containing 14·3 g of the hydrated salt per litre was found to be equivalent to 24·9 cm^3 of 0·1 N sulphuric acid. Find the number of molecules of water of crystallization of the hydrate. [10]

9. 2·10 g of ammonium sulphate (pure) were treated with 100 cm^3 of sodium hydroxide solution (40 g/l) and the mixture heated to expel ammonia. It was cooled and diluted to 250 cm^3 with deionized water. What volume of 0·2 N sulphuric acid would be required to neutralize 25 cm^3 of this solution? [34·1 cm^3]

10. If 30·0 cm^3 of decinormal hydrochloric acid were exactly neutralized by 25·0 cm^3 of a solution which contained 12·0 g/l of a base, calculate the equivalent weight of the base. [100]

11. Find the volume of molar sodium hydroxide solution required to precipitate the copper (as oxide) from a solution prepared by dissolving 3 g of cupric sulphate pentahydrate in water. [24 cm^3]

12. 25 cm^3 of a solution of NaOH, containing 2 g/l, were neutralized by 10 cm^3 of a solution of H_2SO_4. Find (*a*) the weight of H_2SO_4 per litre of solution, (*b*) the volume of water which must be added to a litre of the H_2SO_4 solution in order to make its concentration 4·9 g/l. [6·125 g, 250 cm^3]

13. A sample of marble (0·72 g) was reacted with 25 cm^3 of N HCl and the resulting solution made to 100 cm^3 with deionized water. When 25 cm^3 of this solution were titrated with sodium hydroxide solution, 31·5 cm^3 of 0·1 N NaOH were required for neutralization. Find the percentage of $CaCO_3$ in the marble. [86·1]

14. Describe how you would determine the equivalent weight of zinc by volumetric analysis.

15. Define the terms (*a*) standard solution, (*b*) molar solution. How would you prepare a solution of sodium hydroxide which is approximately 0·1 N and find its exact concentration? (NaOH is hygroscopic.)

16. If you are provided with a pure specimen of a solid acid and N NaOH solution, describe carefully how you would determine the equivalent weight of the acid.

17. A mixture (1·44 g) of sodium carbonate decahydrate and sodium bicarbonate needed 9·25 cm^3 of 1·2 N hydrochloric acid for neutralization. What is the percentage of each substance present in the mixture? [59·2% $Na_2CO_3.10H_2O$, 40·8% $NaHCO_3$]

18 Qualitative Analysis

18.1 GAS TESTING

Procedure

1. Action of heat on dry solid in ignition tube.
2. Action of dil. hydrochloric acid on substance.
3. Action of dil. sodium hydroxide solution (for ammonia only).
4. Action of a small quantity of conc. sulphuric acid on substance.

Table 18.1

Property tested	*Gas*	*Observations*
1. Colour	Cl_2	Green/yellow
	HCl	Colourless, but gives white fumes in air
	NO_2	Brown
2. Smell	NH_3 Cl_2 HCl H_2S NO_2 SO_2	They all have smells and you will have to learn to recognize them by generating the gases from known compounds
3. Moist blue and red litmus	NH_3	Red litmus goes blue
	Cl_2	Blue litmus turned red, then bleached
	HCl	Blue litmus goes red
	NO_2	Blue litmus goes red
	SO_2	Blue litmus goes red
4. Combustion	CO	Burns with a blue flame to give CO_2
	H_2	Explodes with a shrill 'pop'
	H_2S	Burns with a blue flame and deposits sulphur
5. Glowing splint inserted in gas	O_2	Rekindles splint
	N_2O	Rekindles splint

Table 18.2

Gas	*Method of identification*
1. NH_3	Smell, colourless, moist red litmus → blue, fumes of NH_4Cl with conc. HCl, brown ppt. with Nessler's reagent
2. CO_2	No smell, colourless, limewater → milky
3. CO	No smell, colourless, burns with blue flame to give carbon dioxide (limewater test)
4. Cl_2	Choking smell, pale green, moist blue litmus → red → bleached, KI paper → brown
5. H_2	No smell, colourless, explodes with 'pop' (if mixed with air) when flame applied
6. HCl	Irritating smell, colourless (but fumes), moist blue litmus → red, white fumes with ammonia (vapour from 0·88 ammonia bottle)
7. H_2S	Smells of rotten eggs, colourless, burns with blue flame and deposits sulphur, lead acetate paper → black, potassium permanganate paper → colourless, potassium dichromate paper → green
8. NO_2	Brown gas, choking smell, moist blue litmus → red
9. SO_2	Irritating smell, colourless, potassium permanganate paper → colourless, potassium dichromate paper → green
Water vapour	Colourless, odourless, condenses to liquid water on cooler parts of tube, white anhydrous $CuSO_4$ → blue

18.2 TESTS FOR ANIONS (ACIDIC RADICALS, NON-METALLIC RADICALS)

The presence of simple acid radicals in a substance may be detected by the following tests.

(*a*) *Carbonate* (see 10.12). Treat the solid substance or a solution of it in water with dilute nitric acid. Evolution of carbon dioxide (test by limewater) indicates a carbonate.

(*b*) *Chloride* (see 13.4). Treat a solution of the substance in distilled water (why not tap water?) with dilute nitric acid and a solution of silver nitrate. A white precipitate—darkening on exposure to light, and soluble in excess ammonia solution—indicates a chloride.

(*c*) *Sulphate* (see 8.8). Treat a solution of the substance in distilled water with dilute hydrochloric acid and a solution of barium chloride. A white precipitate indicates a sulphate.

(*d*) *Sulphite* (see 8.6).

- (i) Treat the solid substance or a solution of it in water with dilute nitric acid. Warm. Evolution of sulphur dioxide indicates a sulphite.
- (ii) Treat a solution of the substance in distilled water with a solution of barium chloride. A white precipitate—soluble in dilute hydrochloric acid—indicates a sulphite.

(*e*) *Nitrate*. The test for a nitrate is known as the *brown ring test* (see 9.9). It may be carried out in two ways.

- (i) To a solution of the suspected nitrate in distilled water add an equal volume of a solution of ferrous sulphate. Hold the tube at an angle of 45° to the horizontal and add concentrated sulphuric acid slowly so that it sinks to the bottom and forms a lower layer. The formation of a brown ring at the junction of the two layers indicates a nitrate.
- (ii) To 1 cm^3 of concentrated sulphuric acid in a test tube add 2–4 drops of the suspected nitrate solution. Shake thoroughly and cool under the tap. Now pour this mixture slowly down the side of another tube containing 2 cm^3 of ferrous sulphate solution and held at an angle of 45° to the horizontal. The formation of a brown ring at the junction of the two liquid layers confirms the presence of a nitrate.

(*f*) *Nitrite* (see 9.10).

(*g*) *Phosphate* (see 11.4).

(*h*) *Bromide* (see 13.5).

(*i*) *Iodide* (see 13.9).

N.B.

Precipitate	*Colour*	*Solubility in dilute ammonia solution*
Silver iodide	Yellow	Insoluble
Silver bromide	Cream	Partially soluble
Silver chloride	White	Soluble

18.3 TESTS FOR CATIONS (METALLIC RADICALS)

These tests apply only when there is one metallic radical in the solid or in solution.

(a) Flame tests

A clean, hot platinum or nickel wire is dipped into the substance moistened with a little concentrated hydrochloric acid, and the wire is then held in the extreme edge of the bunsen flame (air holes open).

Table 18.3

Radical	*Flame colour*	*Viewed through cobalt glass*
Barium	Apple green	Green
Calcium	Brick red	Light green
Copper	Blue/green	Blue/green
Potassium	Lilac	Crimson
Sodium	Intense yellow	Yellow colour cut out
Strontium	Crimson	Crimson

(b) With sodium hydroxide solution

1. Warm the solid with sodium hydroxide solution. Evolution of ammonia confirms the ammonium ion NH_4^+.
2. Treat a clear solution of the substance in deionized water, or in dilute hydrochloric acid if it does not dissolve in water, with sodium hydroxide solution (a little at a time until the solution is alkaline). If a precipitate forms, add excess alkali and see if the precipitate redissolves.

Table 18.4

Metallic radical	*Hydroxide precipitated*
1. Calcium 2. Magnesium	White $Ca(OH)_2$ or $Mg(OH)_2$, insoluble in excess NaOH
3. Aluminium 4. Zinc 5. Lead	White $Al(OH)_3$, $Zn(OH)_2$, $Pb(OH)_2$, soluble in excess NaOH to give $NaAlO_2$, Na_2ZnO_2 or Na_2PbO_2
6. Ferrous iron 7. Ferric iron 8. Cupric copper	Green $Fe(OH)_2$ Brown $Fe(OH)_3$ Blue $Cu(OH)_2$ insoluble in excess NaOH

In order to distinguish between Al^{+++} and Zn^{++} ions in solution, add ammonia solution drop by drop and then an excess.

Al^{+++} → white ppt of $Al(OH)_3$, insoluble in excess reagent
Zn^{++} → white ppt of $Zn(OH)_2$, soluble in excess to give $Zn(NH_3)_4^{++}$ ions

If ammonia solution is added to a solution containing Cu^{++} ions:

$Cu^{++} \rightarrow$ blue ppt of $Cu(OH)_2$, soluble in excess to give deep blue solution containing $Cu(NH_3)_4^{++}$ ions

An extra test for Pb^{++} ions is that, with a solution containing iodide ions, a yellow precipitate of lead iodide is formed. Also, with a solution containing sulphate ions, a white precipitate of lead sulphate is formed. Also, with a solution containing chloride ions, a white precipitate of lead chloride is formed (much more soluble in hot water than in cold).

Lead chromate $PbCrO_4$ (yellow) is precipitated when solutions containing Pb^{++} and CrO_4^{--} ions are mixed.

(c) Distinction between ferrous and ferric ions

Table 18.5

Test	*Fe^{++}*	*Fe^{+++}*
1. Colour of aq. soln	Pale green	Yellow
2. NaOH soln	Green $Fe(OH)_2\downarrow$	Brown $Fe(OH)_3\downarrow$
3. Ammonium thiocyanate soln	No colouration, but as it is so sensitive, there is generally a faint pink colour if any Fe^{+++} ions are present at all	Blood red colouration
4. Potassium ferricyanide ($K_3Fe(CN)_6$) soln	Blue ppt	Green colouration
5. Potassium ferrocyanide ($K_4Fe(CN)_6$) soln	Pale blue ppt	Blue ppt

(d) Charcoal block test

Place a little of the solid (mixed with anhydrous sodium carbonate) in a depression in the surface of the block and direct a small luminous bunsen flame on to the mixture with a blowpipe.

If the residue is white, it generally indicates that a white oxide is formed which cannot be reduced by carbon at the temperature used, e.g. MgO, Al_2O_3. If the white mass is moistened with cobaltous nitrate solution and the blowpipe redirected on to it, a coloured substance may be formed; blue indicates aluminium, bright green indicates zinc, pale pink indicates magnesium.

Table 18.6

Metal	*Product*
1. Zn	Crust of ZnO, yellow when hot, white when cold
2. Pb	Crust of PbO, red when hot, yellow when cold; globules of Pb may also be formed
3. Cu	Dark red scales of Cu
4. Sn	Hard white beads of tin formed

18.4 QUESTIONS

1. Give one use of each of the following reagents in the laboratory: silver nitrate, ferrous sulphate, potassium iodide, ammonia solution, potassium ferrocyanide, lead acetate.
2. Describe what you would observe when the following are heated, naming the products, and stating how gases evolved may be identified: potassium nitrate, ferrous sulphate crystals, mercuric oxide, cupric nitrate.
3. Describe the tests for the following ions in solution: Fe^{++}, Al^{+++}, Zn^{++}, Cu^{++}, SO_4^{--}, Cl^-, I^-, NO_3^-, HCO_3^-.

19 Concerning Metals

For the occurrence, extraction and chemical properties of metals, see chapter 5.

19.1 USES OF METALS

The uses of metals are governed, to a large extent, by their physical properties.

Sodium—extraction of titanium, making lead tetra-ethyl which is used as 'antiknock' in petrol, in heat-exchange systems of atomic reactors, and (as an amalgam) as a reducing agent in organic chemistry.

Calcium—as a deoxidizer in making alloys, removing the last traces of water from organic liquids, reducing agent for many oxides, minor constituent of some alloys, desulphurizer of petroleum fractions.

Magnesium—flash powders, reducing agent (e.g. reduction of UF_4 to uranium), making important organic compounds called Grignard reagents, and making light alloys (e.g. magnalium Mg 30%, Al 70%) used in aircraft construction.

Aluminium—making alloys (e.g. duralumin, Al with 4% Cu) for use in aircraft construction and watercraft construction, as a structural metal (e.g. roofs), making electrical apparatus (grid networks, condenser plates, sheathing electrical cables), making food containers and cooking utensils; the alloys have great tensile strength.

Zinc—galvanizing iron, making alloys (e.g. brass Cu/Zn), as a building material and for die-casting.

Iron—making steel.

Tin—making tinplate (e.g. cleaning mild steel with dilute sulphuric acid and dipping it into molten tin), making alloys (e.g. bronze Cu/Sn, solder Pb/Sn, type metal Pb/Sn/Sb) and for making tinfoil.

Lead—making alloys (e.g. solder, pewter, type metal), making lead shot (lead alloyed with a little arsenic), roofing and making lead pipes.

Copper—making water and steam pipes, roofing metal, making cooking utensils, telegraph and telephone wires, electric cables and electrotype. It is often used as an alloy, e.g. bronze (92% Cu, 8% Sn), phosphor bronze (90% Cu, 10% Sn, trace P), monel metal (68% Ni, 30% Cu, 1% Fe, 1% Mn), constantan (60% Cu, 40% Ni) brass (70% Cu, 30% Zn).

Mercury—making barometers, thermometers, electrical contacts, mercury-vapour lamps, high vacuum pumps, making amalgams (rub-

Table 19.1

Physical properties of metals

Metal	*M.P.* (°*C*)	*B.P.* (°*C*)	*Density* *g*/cm³	*Conductivity* *Thermal*	*Electrical*	*Particular physical property*	*Particular use*
Na	97	880	0·97	Good	Good	—	—
Ca	810	1240	1·55	Good	Good	—	—
Mg	651	1110	1·74	Good	Good	Low density	Light alloys
Al	660	1800	2·70	Good	Good	Low density, good conductivity	Light alloys. Cooking utensils. Electrical equipment
Zn	419	907	7·14	Good	Good	Low m.p.	Alloys
Fe	1535	3000	7·86	Fair	Fair	Magnetic	Dynamos and motors
Pb	328	1620	11·37	Fair	Fair	High density. Low m.p.	Heavy objects. Alloys
Cu	1083	2310	8·193	V. good	V. good	V. good conductor	Boilers. Electrical components
Hg	−39	357	13·55	Poor	Poor	High density	Barometers

bing a metal with Hg, liberating a metal at a Hg cathode, or adding the metal to a solution of $HgCl_2$), and in the Castner-Kellner cell (see 3.4).

Silver—silver plating, alloys (e.g. standard silver, Ag 92·5%, Cu 7·5%), making silver mirrors, making special components of electrical circuits (e.g. condensers in deaf-aids) and (as Ag^+) as a standard in volumetric analysis.

19.2 SODIUM HYDROXIDE NaOH

This is manufactured by the Castner-Kellner cell (3.4) or by Gossage's process, in which milk of lime (calcium hydroxide made into a thin paste with water) is added to a boiling 10 per cent solution of washing soda.

$$2Na^+ + CO_3^{--} + Ca^{++} + 2OH^- \rightarrow CaCO_3\downarrow + 2Na^+ + 2OH^-$$

Gossage's process can work because the solubility product (see 8.5) of calcium carbonate is much smaller than that of calcium hydroxide at a given temperature.

The solution remaining after filtration is evaporated to dryness.

It is known as caustic soda since it corrodes the skin—it feels soapy.

It dissolves in water with the evolution of much heat, forming sodium hydroxide solution, a strong alkali. If exposed to the air, it deliquesces, and then absorbs carbon dioxide forming (eventually) sodium carbonate.

Its aqueous solution can precipitate many metallic hydroxides and some redissolve in excess of the reagent (7.10).

19.3 SODIUM CARBONATE Na_2CO_3

This is made industrially by the Solvay (Ammonia-Soda) process.

The *overall* reaction is:

$$2NaCl + CaCO_3 \rightarrow CaCl_2 + Na_2CO_3$$

Since this cannot be carried out in one stage, the following stages are employed:

(1) *Ammonification of brine*

$$\overbrace{Na^+ + Cl^-} + H_2O + NH_3 \rightarrow \overbrace{Na^+ + Cl^-}\text{ (conc)} + NH_4OH$$

(2) *Carbonation (Solvay tower)*

$$\overbrace{Na^+ + Cl^-} + NH_4OH + CO_2 \rightarrow [\overbrace{Na^+ + Cl^-} + \overbrace{NH_4^+ + HCO_3^-}]$$

$$\downarrow$$

$$NaHCO_3\downarrow + \underset{\substack{\text{ammonium chloride}\\ \text{to stage (5)}}}{\overbrace{NH_4^+ + Cl^-}}$$

Solvay process

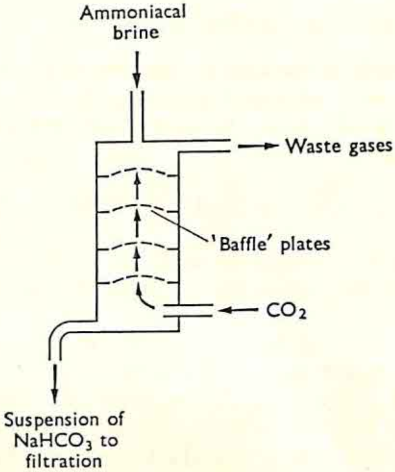


FIG. 19.1

(3) *Conversion of sodium bicarbonate to sodium carbonate*

$$2NaHCO_3 \xrightarrow{\text{heat}} Na_2CO_3 + H_2O + CO_2\uparrow$$

(4) *Lime burning*

$$CaCO_3 \rightleftharpoons CaO + CO_2\uparrow$$

(carbon dioxide to stage (2), calcium oxide to stage (5)).

(5) *Regeneration of ammonia*

$$CaO + H_2O \rightarrow Ca(OH)_2;$$

$$\overbrace{2NH_4^+ + 2Cl^-} + Ca(OH)_2 \xrightarrow{\text{heat}} \overbrace{Ca^{++} + 2Cl^-} + 2H_2O + 2NH_3\uparrow$$

N.B. Calcium chloride is a valuable co-product.

Raw materials: limestone $CaCO_3$, brine NaCl

Sodium bicarbonate has only a slight solubility in water but even this is depressed by the presence of sodium chloride, which provides sodium ions Na^+ (by the law of mass action, this forces sodium bicarbonate to be less soluble).

$$Na^+HCO_3^- \rightleftharpoons Na^+ + HCO_3^-$$
$$\leftarrow \text{addition of } Na^+ \text{ ions}$$

Potassium bicarbonate is much more soluble than sodium bicarbonate and is not precipitated by a Solvay method in which potassium chloride is used instead of sodium chloride.

[Potassium carbonate is made by hydrolysis of the double salt $KHCO_3.MgCO_3.4H_2O$, formed from potassium chloride, magnesium carbonate and carbon dioxide (under pressure).

$$2KHCO_3.MgCO_3.4H_2O \xrightarrow[\text{140°C pressure}]{H_2O} 2MgCO_3\downarrow + K_2CO_3 + 9H_2O + CO_2]$$

A *simpler approach* to the Solvay process is as follows.
The basic equation is:

$$Na^+ + HCO_3^- \rightarrow NaHCO_3\downarrow$$

i.e. the compound of *lowest solubility product* is precipitated.

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \ldots \quad (1)$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^{--} \ldots \quad (2)$$

Ammonia forms ammonium ions

$$NH_3 + H^+ \rightarrow NH_4^+$$

upsetting both the equilibria (1) and (2). Hence the concentration of HCO_3^- ions increases and sodium bicarbonate is precipitated.

N.B. Treat precipitation reactions through the concept of solubility product (see 8.5).

Sodium carbonate is soluble in water and the solution is alkaline to litmus owing to hydrolysis.

$$Na_2CO_3 + 2H_2O \rightleftharpoons \underbrace{\overbrace{2Na^+ + 2OH^-}}_{\text{strong alkali}} + \underbrace{H_2CO_3}_{\text{weak acid}}$$

Sodium carbonate decahydrate is formed when the anhydrous salt is dissolved in water and the solution crystallized. It is efflorescent (see 6.8).

Sodium carbonate reacts with dilute mineral acids to give carbon dioxide.

$$CO_3^{--} + 2H^+ \rightarrow H_2O + CO_2\uparrow$$

Sodium bicarbonate is used in baking powders, when mixed with tartaric acid or sodium dihydrogen phosphate; the carbon dioxide evolved makes bread rise. In baking powders:

1st action: $$2NaHCO_3 \xrightarrow[>100^\circ C]{\text{heat}} Na_2CO_3 + CO_2 + H_2O$$

2nd action: with acid phosphate (or tartaric acid)

$$Na_2CO_3 + 2H^+ \rightarrow CO_2 + H_2O + 2Na^+$$

There is usually also a diluent—often rice flour. Sodium bicarbonate *by itself* is used as baking soda, utilizing the carbon dioxide evolved on heating only. When treated with a dilute acid, it behaves as follows:

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2\uparrow$$
$$(\text{or } NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2\uparrow)$$

When heated, it decomposes as follows:

$$2HCO_3^- \rightarrow CO_3^{--} + H_2O + CO_2\uparrow$$
$$(\text{or } 2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2\uparrow)$$

Many cases of indigestion are due to excess acidity in the stomach and are relieved by taking 'bicarbonate of soda'—sodium bicarbonate.

19.4 SODIUM NITRATE $NaNO_3$

This occurs as Chile saltpetre, the main component of Caliche. The nitrate is extracted by dissolving it out in water and allowing the resulting solution to evaporate in the sun. A co-product is sodium iodate, used to make iodine (see 13.7). Sodium nitrate is used as a fertilizer, and to make potassium nitrate by fractional crystallization.

$$\overbrace{K^+ + Cl^-} + \overbrace{Na^+ + NO_3^-} \rightarrow \underset{\substack{\downarrow \\ \text{crystallizes on} \\ \text{cooling to room} \\ \text{temperature} \\ \text{(after filtering} \\ \text{off NaCl)}}}{\overbrace{K^+ + NO_3^-}} + \underset{\substack{\downarrow \\ \text{crystallized from hot} \\ \text{solution since it is} \\ \text{least soluble of the} \\ \text{4 salts and it can} \\ \text{therefore be filtered} \\ \text{off}}}{\overbrace{Na^+ + Cl^-}}$$

19.5 SODIUM THIOSULPHATE $Na_2S_2O_3$

This is made by boiling sodium sulphite solution with sulphur under slight pressure.

$$SO_3^{--} + S \rightarrow S_2O_3^{--}$$

With dilute acids it gives sulphur dioxide and sulphur.

$$S_2O_3^{--} + 2H^+ \rightarrow SO_2\uparrow + S + H_2O$$

With iodine, it is oxidized to sodium tetrathionate.

$$2S_2O_3^{--} + I_2 \rightarrow 2I^- + S_4O_6^{--}$$

It is used as the 'fixer' HYPO in photography. It 'fixes' the image on the negative by reacting with unchanged silver bromide to form a complex $(Na^+)_3[Ag(S_2O_3)_2]^{---}$, which can be washed away with water.

On heating the hydrated crystals, $Na_2S_2O_3.5H_2O$, and cooling, a supersaturated solution is formed (see 14.1).

On strong heating, it gives sodium sulphate and pentasulphide.

$$4Na_2S_2O_3 \rightarrow 3Na_2SO_4 + Na_2S_5$$

$$\text{or} \quad 4S_2O_3^{--} \rightarrow 3SO_4^{--} + S_5^{--}$$

19.6 SODIUM CHLORIDE NaCl

This is essential to the diet and is used as 'salt' on the table. It is a valuable raw material for making sodium hydroxide and chlorine (3.4), sodium (3.4), sodium carbonate (19.3), sodium sulphate (the reaction, called the Leblanc process, is that once used to manufacture hydrochloric acid (13.4)), and many other sodium compounds.

It occurs in sea water, but it is not always economical to obtain it from this source; it is done, however, on the shores of the Mediterranean and Dead Sea. More often, salt is mined as rock salt, or water is forced into some underground deposit to convert the solid to brine, which can be pumped up to the surface (e.g. in Cheshire).

19.7 POTASSIUM NITRATE (NITRE) KNO_3

This occurs in the soil of several very hot countries, e.g. India. It is manufactured from sodium nitrate (see 19.4). It is used in making gunpowder (sodium nitrate cannot be used as it is deliquescent, whereas potassium nitrate is not), fireworks, and as a fertilizer.

19.8 POTASSIUM CHLORATE $KClO_3$

This is formed when excess chlorine reacts with hot concentrated potassium hydroxide solution (13.3). It can be made from sodium chlorate, which is manufactured from brine (3.4), by reacting it with potassium chloride; on crystallization, potassium chlorate is formed from the mixture.

$$\overbrace{Na^+ + ClO_3^-} + \overbrace{K^+ + Cl^-} \rightarrow \overbrace{Na^+ + Cl^-} + \overbrace{K^+ + ClO_3^-}$$

It is a powerful oxidizing agent. On heating, it gives oxygen and potassium chloride.

$$2KClO_3 \rightarrow 2KCl + 3O_2\uparrow$$

It is used in the manufacture of explosives, matches and fireworks.

19.9 CALCIUM OXIDE CaO

This is commonly called 'quicklime' and is made by heating the carbonate very strongly in a limekiln. Since the decomposition is reversible, carbon dioxide has to be removed by passing air through the kiln (Law of Mass Action). Calcium oxide reacts vigorously with water, with the liberation of much heat, forming 'slaked lime'.

$$CaO + H_2O \rightarrow \underset{\text{slaked lime}}{Ca(OH)_2} \qquad \Delta H = -15 \text{ kilocalories (evolved)}$$

This reaction enables quicklime to be used as a drying agent, e.g. for ammonia.

When heated with coke in an electric furnace at 2000°C, calcium carbide is formed, and this liberates acetylene when reacted with water (see 10.7).

$$CaO + 3C \rightarrow CaC_2 + CO\uparrow$$

$$Ca^{++} + (C{\equiv}C)^{--} + 2H_2O \rightarrow Ca^{++} + 2OH^- + \underset{\text{acetylene}}{H{-}C{\equiv}C{-}H}\uparrow$$

19.10 CALCIUM HYDROXIDE $Ca(OH)_2$

This is made by slaking quicklime. It is slightly soluble in water to give 'lime water', which is alkaline. It is a basic hydroxide, reacting with acids to give Ca^{++} salts but having no reaction with alkalis.

$$Ca(OH)_2 + 2H^+ \rightarrow Ca^{++} + 2H_2O$$

It is used in the laboratory preparation of ammonia, for treating 'acid' soil, for making calcium bisulphite (formed when it reacts with sulphur dioxide in excess) which is used in the manufacture of paper (see 8.4), as whitewash, in many distemper paints, for softening water, and in the manufacture of bleaching powder (13.4).

Calcium hydroxide is used to make *mortar*, which is a mixture of slaked lime with sand. Water is added and, as it evaporates, a hard mass is obtained. In time, the slaked lime is converted to calcium carbonate by carbon dioxide in the air, this helping the mortar to set hard. Sand merely binds together the particles of calcium carbonate.

19.11 CALCIUM CARBONATE $CaCO_3$

This exists in two forms (i.e. it exhibits polymorphism), calcite (stable at lower temperatures) and aragonite (stable at higher temperatures). There is a transition temperature (8.2) at about 400°C. The most important natural sources of calcium carbonate are limestone, marble, iceland spar and chalk (not blackboard chalk, which is usually calcium sulphate). Egg shells, coral rocks, oyster shells also contain it. Calcite is the most common form, but aragonite occurs in shells and coral.

Natural deposits of calcium carbonate give rise to temporary hardness of water, owing to the formation of calcium bicarbonate when rain water flows over the rocks.

Limestone and marble are used for building, and limestone is also used for making quicklime, slaked lime, glass (12.5), sodium carbonate (19.3), steel (19.20) and cement (12.7). Finely-divided calcium carbonate is used for treating acid soils. Chalk is used for making putty, pigments, glass, paper and toothpastes.

19.12 CALCIUM SULPHATE $CaSO_4$

This occurs as Gypsum (the dihydrate) and Anhydrite (the anhydrous salt). Gypsum is one of the salts which cause permanent hardness of water. When Gypsum is heated between 110–130°C, Plaster of Paris, $CaSO_4.\frac{1}{2}H_2O$ or $2CaSO_4.H_2O$, is formed. If water is added, this crystallizes as Gypsum with expansion, thereby filling the crevices in a mould. It is used for making casts, in surgery for setting broken bones, and in constructional plasters. Anhydrite is used in the manufacture of sulphur dioxide (8.6).

19.13 CALCIUM CYANAMIDE CaNCN

This is made by heating calcium carbide in nitrogen.

$$CaC_2 + N_2 \rightarrow CaNCN + C$$

It is a valuable fertilizer ('nitrolime' is the calcium cyanamide/carbon mixture). The calcium cyanamide is slowly hydrolysed to ammonia by soil water.

$$CaNCN + 3H_2O \rightarrow 2NH_3 + CaCO_3$$
$$(\text{or } NCN^{--} + 3H_2O \rightarrow 2NH_3 + CO_3^{--})$$

The ammonia is absorbed into the soil and the calcium carbonate is, of course, beneficial also.

19.14 ALUMINIUM OXIDE (ALUMINA) Al_2O_3

This occurs naturally as Bauxite and, in slightly impure forms, in the gemstones rubies and sapphires. The ordinary oxide is a white powder.

The metal can be obtained from alumina only by electrolysis, since the aluminium/oxygen bond is so strong. Aluminium is used in *thermite* reduction owing to this stability of the aluminium/oxygen bond, for example:

$$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr \quad \text{(manufacture of chromium)}$$
$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe$$

Thermite process

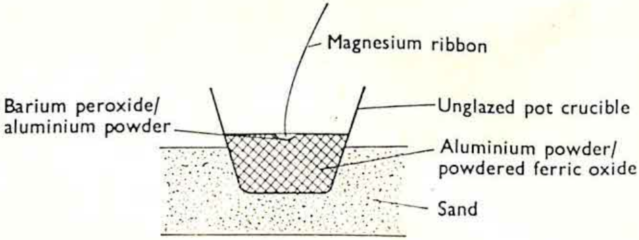


FIG. 19.2

The process can be demonstrated in the laboratory using the apparatus of fig. 19.2.

On cooling the reaction mixture, the iron remains as a grey mass. The temperature reached may be well over 3000°C.

Alumina is insoluble in water, but reacts with both acids and alkalis to give salts, i.e. it is amphoteric.

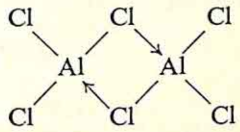
19.15 ALUMINIUM CHLORIDE $AlCl_3$

This can be made by dissolving aluminium or its hydroxide in hydrochloric acid (this gives the hydrate) or by heating aluminium turnings in a stream of dry chlorine or hydrogen chloride (fig. 13.2).

The formula in the vapour state below 400°C is Al_2Cl_6 (association of the simple molecules) but this dissociates above 400°C.

$$Al_2Cl_6 \rightleftharpoons 2AlCl_3$$

The dimer has a structure containing co-ordinate covalent bonds.



Anhydrous aluminium chloride is a covalent compound. The liquid is only a feeble electrical conductor. The solid is soluble in water but readily hydrolysed by it.

$$AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3HCl$$

It also fumes in moist air. The solid is soluble in organic solvents, e.g. chloroform, carbon tetrachloride, which is typical of the property of a covalent compound.

Anhydrous aluminium chloride is a Friedel-Crafts catalyst (see 10.8).

In aqueous solution, the hydrated ion $Al(H_2O)_6^{+++}$ is present.

N.B. Aluminium fluoride AlF_3 is an ionic compound, containing Al^{+++} and F^- ions, although the vapour may contain Al_2F_6 molecules. The reason for the difference in properties between this and the chloride is due to the small size of the fluoride ion F^- compared with the chloride ion Cl^- (see a more advanced textbook).

19.16 ALUMINIUM SULPHATE $Al_2(SO_4)_3$

This can be obtained by reacting alumina with sulphuric acid. It is manufactured by reacting Bauxite with sulphuric acid. It crystallizes with 18 molecules of water attached. It is used in the manufacture of foam fire-extinguishers, waterproofing cloth, precipitating colloids (see 14.4), and for preparing many Alums, e.g. Potash alum

$$K^+Al^{+++}(SO_4^{--})_2.12H_2O \quad \text{or} \quad (K^+)_2SO_4^{--}.(Al^{+++})_2(SO_4^{--})_3.24H_2O$$

This is obtained when solutions containing equi-formula weight quantities of potassium sulphate and aluminium sulphate are mixed and crystallized.

Another method of preparation of Potash alum is to (1) react excess aluminium with warm potassium hydroxide solution forming the aluminate, (2) add the requisite quantity of sulphuric acid, this first precipitating aluminium hydroxide and then dissolving it.

$$2Al + \overbrace{2K^+ + 2OH^-} + 2H_2O \rightarrow \overbrace{2K^+ + 2AlO_2^-} + 3H_2\uparrow$$

$$\overbrace{2K^+ + 2AlO_2^-} + \overbrace{8H^+ + 4SO_4^{--}} \rightarrow 4H_2O +$$

$$\underbrace{\begin{array}{ccc} \overbrace{2K^+ + SO_4^{--}} & + & \overbrace{2Al^{+++} + 3SO_4^{--}} \\ \downarrow & & \downarrow \\ K_2SO_4 & & Al_2(SO_4)_3 \end{array}}_{\begin{array}{c}\downarrow \text{crystallization} \\ KAl(SO_4)_2 . 12H_2O\end{array}}$$

[In $KAlO_2$, there is the correct K/Al proportion for alum formation.]

19.17 ALUMINIUM CARBIDE Al_4C_3

This reacts with water to give methane (see 10.4).

$$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4\uparrow$$

19.18 ZINC CHLORIDE $ZnCl_2$

This is made by reacting zinc, zinc oxide, hydroxide or carbonate with hydrochloric acid. The anhydrous compound is made by heating zinc in dry chlorine or hydrogen chloride.

If the solution is boiled, or if a hydrate is heated, hydrolysis to a basic salt occurs.

$$ZnCl_2 + H_2O \rightleftharpoons Zn(OH)Cl + HCl$$

This shows a measure of covalency in the bonds of zinc chloride, compared say with sodium chloride. Anhydrous zinc chloride is also a feeble conductor in the molten state, is soluble in many organic solvents, and is fairly volatile.

19.19 ZINC SULPHIDE ZnS

This occurs as Zinc Blende, which is used in the manufacture of the metal (table 5.2). Its crystal structure resembles that of diamond (fig. 10.1) with zinc and sulphur atoms replacing carbon atoms.

It is precipitated when hydrogen sulphide is passed into an alkaline solution of a zinc salt (8.5). It reacts with dilute mineral acids giving hydrogen sulphide.

$$ZnS + 2H^+ \rightarrow Zn^{++} + H_2S\uparrow$$

19.20 WROUGHT IRON AND STEEL

Wrought iron is made by heating pig iron with Haematite, the latter oxidizing some of the carbon to carbon dioxide. It is used to make fire guards, chains, etc.

Steel is obtained from pig iron by removal of some of the carbon and other impurities. It is more commonly used than wrought iron since its properties can be varied by varying the carbon content and in other ways, and it is more easily made.

(a) Bessemer process

Air (or air enriched with oxygen, since nitrogen in air makes steel brittle) is passed through a charge of molten pig iron. If oxygen alone is used, it is diluted with steam or carbon dioxide. The cold air (or oxygen) reacts with carbon and other impurities, generating heat (the temperature may be 1300–1600°C), and gaseous products burn at the mouth of the converter (the 'blow'). The oxides of silicon and manganese form a slag. Acidic oxides such as SO_2, P_2O_5 react with the basic lining and the lining, when eventually removed, forms a useful fertilizer.

Making steel

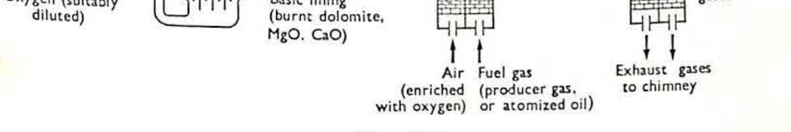

Bessemer
Open-hearth (Siemens-Martin)
Gases (e.g. CO) burn
Air (enriched with oxygen) or Oxygen (suitably diluted)
Charge
Basic lining (burnt dolomite, MgO. CaO)
Hot firebricks
Basic hearth
Bricks heated by exhaust gases
Air (enriched with oxygen)
Fuel gas (producer gas, or atomized oil)
Exhaust gases to chimney

FIG. 19.3

(b) Open hearth (Siemens-Martin) process

The charge is a mixture of pig iron, scrap steel and haematite which is heated by passing a mixture of air (or oxygen-enriched air) and producer gas (or atomized oil) over it. Carbon and other impurities in the pig iron react with oxygen in the Haematite to form iron, which stays in the bath, and gaseous products escape.

A heat-interchanger system is used. After the second set of firebricks has been heated, the direction of flow of gases through the furnace is reversed so that the first set of bricks is heated, and so on.

It is slower than the Bessemer process, but larger charges can be handled.

(c) Electrical processes

These are expensive, but are capable of closer control than the other methods as there are no oxidizing gases present.

In the *arc method*, a temperature of about 3500°C is generated in a charge similar to that of the Open hearth by striking an arc across graphite electrodes.

In the *induction furnace*, the heat in the charge is generated by an alternating current flowing through a copper coil—an alternating current is induced in the iron of the charge which raises the temperature until the whole is molten.

Types of steel

(*a*) Mild steel (0·1–0·5 per cent carbon).
(*b*) Hard steel (0·5–1·5 per cent carbon).
(*c*) Alloy steel (about 1 per cent carbon plus varying amounts of other alloying elements).

[Note that pig (cast) iron from the Blast Furnace contains about 4·5–5·0 per cent of carbon, in addition to other impurities such as silicon, sulphur, phosphorus and manganese.]

Mild steels are used to make nuts, bolts, car bodies, girders, steel pipes, 'tin' plate, etc.

Hard steels are used mainly to make tools.

Alloy steels have various uses, e.g. stainless steels contain chromium, permanent-magnet steels contain cobalt, steel for high-speed drills contains tungsten, acid-resistant steels contain molybdenum, spring steels contain silicon, etc.

When hard or alloy (but not mild) steel is heated to red-heat and cooled rapidly in cold water, it is hardened (but made brittle). The brittleness can be reduced by tempering (specialized heat treatment). Iron itself is not hardened in this way.

19.21 OXIDES OF IRON

Three oxides are known, ferrous oxide FeO, ferric oxide Fe_2O_3 and ferroso-ferric oxide Fe_3O_4. Ferrous oxide can be written simply as $Fe^{++}O^{--}$, but it really has a structure which cannot be represented by a clear-cut formula (this type of compound is called non-stoichiometric). Ferric oxide can be treated as $(Fe^{+++})_2(O^{--})_3$. Ferroso-ferric oxide can be treated as $Fe^{++}(FeO_2^-)_2$. They are all basic oxides.

Ferrous oxide is prepared by heating ferrous oxalate in the absence of air.

$$Fe^{++}C_2O_4^{--} \rightarrow Fe^{++}O^{--} + CO\uparrow + CO_2\uparrow$$

Ferrous oxide is spontaneously inflammable in air.

Ferric oxide can be made by heating ferric hydroxide $Fe^{+++}(OH^-)_3$.

$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O$$

It is also made by heating ferrous sulphate.

$$2Fe^{++}SO_4^{--} \rightarrow Fe_2O_3 + SO_2\uparrow + SO_3\uparrow$$

It occurs naturally as haematite.

Ferroso-ferric oxide is made by passing steam over red-hot iron.

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$

It occurs naturally in the magnetic mineral magnetite (lodestone). With acids, it gives a mixture of ferrous and ferric salts.

19.22 HYDROXIDES OF IRON

Ferrous hydroxide $Fe^{++}(OH^-)_2$ is formed as a green precipitate (said to be white if all air is excluded from the apparatus) when a solution containing hydroxyl ions is added to one containing ferrous ions.

$$Fe^{++} + 2OH^- \rightarrow Fe(OH)_2\downarrow$$

Ferric hydroxide $Fe^{+++}(OH^-)_3$ is formed as a red/brown gelatinous precipitate when a solution containing hydroxyl ions is added to one containing ferric ions.

$$Fe^{+++} + 3OH^- \rightarrow Fe(OH)_3\downarrow$$

Both hydroxides are basic.

19.23 CHLORIDES OF IRON

Ferrous chloride is made by passing dry hydrogen chloride over hot iron wire.

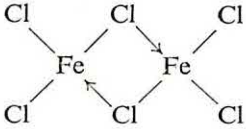
$$Fe + 2HCl \rightarrow FeCl_2 + H_2$$

It dissolves in water to give a solution containing hydrated ferrous ions, $[Fe(H_2O)_xCl_2]^+$, which have a green colour.

Ferric chloride is made by passing dry chlorine over hot iron wire.

$$2Fe + 3Cl_2 \rightarrow Fe_2Cl_6$$

It exists as covalent double molecules in the vapour state (cf. Al_2Cl_6),



but dissolves in water to give a solution containing hydrated ferric ions, $[Fe(H_2O)_xCl_2]^+$, which have a yellow colour.

19.24 THE OXIDES OF LEAD

Lead monoxide PbO is made by heating lead nitrate, carbonate, or any higher oxide of lead. On an industrial scale, it is made by heating lead in air.

$$2Pb + O_2 \rightarrow 2PbO$$

It is formed as a yellow powder ('massicot'). If this is fused, allowed to cool, and powdered, a reddish-brown form called 'litharge' is formed.

It is amphoteric, reacting with acids to form plumbous salts and with solutions of caustic alkalis to form plumbites, for example:

$$PbO + \overbrace{2H^+ + 2NO_3^-} \rightarrow \overbrace{Pb^{++} + 2NO_3^-} + H_2O$$

$$PbO + \overbrace{2Na^+ + 2OH^-} \rightarrow \overbrace{2Na^+ + PbO_2^{--}} + H_2O$$

If heated in air at about 450°C it forms red lead.

$$6PbO + O_2 \rightleftharpoons 2Pb_3O_4$$

At higher temperatures, dissociation of the red lead occurs.

Red lead, Pb_3O_4, is used in making glass and in some red paints (as a pigment). Chemically, it behaves at $2PbO.PbO_2$, i.e. a mixed oxide. With dilute nitric acid it gives lead dioxide as a precipitate.

$$\left\{\begin{array}{l} 2PbO + 4HNO_3 \rightarrow \overbrace{2Pb^{++} + 4NO_3^-} + 2H_2O \\ PbO_2 \text{ has no reaction with dilute nitric acid} \end{array}\right.$$

hence:

$$Pb_3O_4 + 4HNO_3 \rightarrow \overbrace{2Pb^{++} + 4NO_3^-} + PbO_2\downarrow + 2H_2O$$

Lead dioxide, PbO_2, is a brown powder which is a powerful oxidizing agent (cf. MnO_2). It oxidizes hot concentrated hydrochloric acid to chlorine.

$$PbO_2 + 4HCl \rightarrow PbCl_2 + 2H_2O + Cl_2\uparrow$$

When heated above 300°C it decomposes.

$$2PbO_2 \rightarrow 2PbO + O_2$$

19.25 PLUMBOUS CHLORIDE $PbCl_2$

This is precipitated when a solution containing Cl^- ions is added to one containing Pb^{++} ions.

$$Pb^{++} + 2Cl^- \rightarrow PbCl_2\downarrow$$

It is *much* more soluble in hot water than in cold. It dissolves in concentrated hydrochloric acid forming chloroplumbous acid, $(H^+)_2PbCl_4^{--}$.

19.26 PLUMBOUS IODIDE PbI_2

This is precipitated as a yellow solid when a solution containing I^- ions is added to one containing Pb^{++} ions.

$$Pb^{++} + 2I^- \rightarrow PbI_2\downarrow$$

It is much more soluble in hot water than cold. If hot potassium iodide solution is added to a hot solution of a plumbous salt, and the mixture cooled, the iodide is formed as lustrous golden spangles.

19.27 CUPRIC OXIDE CuO

This is a black solid, formed when cupric hydroxide, carbonate or nitrate is heated. It is basic, and hygroscopic. It is used in organic analysis as an oxidizing agent.

19.28 CUPROUS OXIDE Cu_2O

This is formed as a red solid when Fehling's solution (effectively cupric hydroxide) is boiled with an Aldehyde, a compound of general formula R.CHO, where R is a group such as alkyl (e.g. acetaldehyde, CH_3CHO, glucose, $C_6H_{12}O_6$), for example:

$$\text{'}2Cu(OH)_2\text{'} + \underset{\text{aldehyde}}{R.CHO} \rightarrow Cu_2O\downarrow + \underset{\text{acid}}{R.COOH} + H_2O$$

It is basic, reacting with acid to give cuprous salts, or cupric salts plus copper if the cuprous salts are not stable.

19.29 CUPRIC CHLORIDE $CuCl_2$

This is made by reacting cupric oxide, hydroxide or carbonate with dilute hydrochloric acid, and crystallizes as a dihydrate. It is a greenish solid which gives a blue aqueous solution. This is because the blue colour of a cupric salt is due to the $Cu(H_2O)_4{}^{++}$ ion;* in the crystal, this ion cannot be present, but it can be formed in aqueous solution where there are many water molecules.

The anhydrous salt is formed when copper is heated gently in chlorine. If it is heated strongly, cuprous chloride is formed.

$$2CuCl_2 \rightarrow 2CuCl + Cl_2\uparrow$$

Both the hydrate and anhydrous salt are very deliquescent.

19.30 CUPROUS CHLORIDE CuCl

This can be made by the reduction of cupric chloride with copper.

$$\overparen{Cu^{++} + 2Cl^-} + Cu \xrightarrow{\text{heat}} \underset{(2CuCl)}{\overparen{2Cu^+ + 2Cl^-}}$$

Cupric oxide is dissolved in concentrated hydrochloric acid and the solution is warmed with copper until the blue colour has disappeared. If the solution is then poured into air-free distilled (or deionized) water, cuprous chloride is precipitated as a white solid.

A more convenient method is by reduction of a mixed solution of cupric sulphate and sodium chloride (i.e. Cu^{++} and $2Cl^-$ ions present) with sulphur dioxide.

$$2Cu^{++} + 2Cl^- + 2H_2O + SO_2 \rightarrow SO_4^{--} + 4H^+ + 2CuCl\downarrow$$

---

* Some authors give the formula of the hydrated cupric ion as $Cu(H_2O)_6{}^{++}$.

It is soluble in ammonia solution to give a colourless solution called ammoniacal cuprous chloride (often blue owing to atmospheric oxidation). This absorbs carbon monoxide (see 10.12), and acetylene (see 10.7).

19.31 CUPRIC SULPHATE (BLUE VITRIOL) $CuSO_4$

This is formed when the oxide, hydroxide or carbonate is reacted with dilute sulphuric acid (6.8). It crystallizes as the blue pentahydrate. When heated at about 110°C, it loses 4 of its molecules of water to give the monohydrate. At about 300°C, it gives anhydrous cupric sulphate (white). At even higher temperatures, it gives the oxide and sulphur trioxide.

$$CuSO_4 \rightarrow CuO + SO_3\uparrow$$

Cupric sulphate is used in the refining of copper and in copper plating (see 3.4). It is also used in agricultural sprays (e.g. Bordeaux mixture) which are used to control fungus diseases of crops such as potatoes.

19.32 CUPRIC SULPHIDE CuS

This is precipitated as a black solid when hydrogen sulphide is passed into a solution containing Cu^{++} ions. It occurs naturally as Copper pyrites CuS.FeS.

On strong heating, it gives cuprous sulphide and sulphur.

$$2CuS \rightarrow Cu_2S + S$$

When exposed to damp air, it is slowly oxidized to the sulphate.

$$CuS + 2O_2 \rightarrow CuSO_4$$

19.33 CUPROUS IODIDE CuI

This is precipitated as a white crystalline solid when a solution containing iodide ions (e.g. potassium iodide) is added to a solution containing cupric ions. The brown colour of the iodine is removed by reacting it with sodium thiosulphate solution.

$$2Cu^{++} + 4I^- \rightarrow 2CuI\downarrow + I_2$$

19.34 MERCURIC CHLORIDE $HgCl_2$ ('corrosive sublimate')

This is formed by sublimation from a mixture of mercuric sulphate and sodium chloride.

$$HgSO_4 + 2NaCl \xrightarrow{\text{heat}} HgCl_2\uparrow + Na_2SO_4$$

It is soluble in water, and can be reduced by stannous chloride to give a white precipitate of mercurous chloride (turning grey owing to the formation of mercury).

$$2Hg^{++} + Sn^{++} \rightarrow \underset{\displaystyle Hg_2Cl_2}{\underset{\downarrow 2Cl^-}{Hg_2^{++}}} + Sn^{++++} \qquad \text{(white ppt)}$$

$$Hg_2^{++} + Sn^{++} \rightarrow 2Hg + Sn^{++++} \qquad \text{(turns grey)}$$

19.35 MERCUROUS CHLORIDE Hg_2Cl_2 ('calomel')

This is precipitated as a white solid when a solution containing Cl^- ions is added to mercurous nitrate solution. It readily sublimes on heating.

19.36 MERCURIC IODIDE HgI_2

This is formed as an orange precipitate when a solution containing iodide ions (e.g. potassium iodide) is added to a solution containing mercuric ions.

$$Hg^{++} + 2I^- \rightarrow HgI_2\downarrow$$

It is soluble in excess potassium iodide solution forming potassium mercuri-iodide (colourless solution).

$$2K^+ + 2I^- + HgI_2 \rightarrow 2K^+ + HgI_4^{--}$$

An alkaline solution of this is called Nessler's reagent and gives a brown precipitate with ammonia.

19.37 NITRATES OF MERCURY

Mercurous nitrate $Hg_2(NO_3)_2$ is the only mercurous salt which is readily soluble in water, and it is therefore used to prepare other mercurous salts by precipitation. It is made by reacting mercury with dilute nitric acid.

$$6Hg + 8HNO_3 \rightarrow \overbrace{3Hg_2^{++} + 6NO_3^-} + 2NO\uparrow + 4H_2O$$

Mercuric nitrate $Hg(NO_3)_2$ is also soluble in water. It is made by reacting mercury with concentrated nitric acid, or mercuric oxide with dilute nitric acid.

$$Hg + 4HNO_3 \rightarrow \overbrace{Hg^{++} + 2NO_3^-} + 2NO_2\uparrow + 2H_2O$$

When either nitrate is heated, the products are entirely volatile, for example:

$$Hg(NO_3)_2 \rightarrow Hg\uparrow + 2NO_2\uparrow + O_2\uparrow$$

19.38 QUESTIONS

1. Give an account of the Solvay process for the manufacture of sodium carbonate. Explain how hard water may be softened by the addition of washing soda.
2. Describe the preparation of sodium chlorate from sodium chloride. How may sodium chlorate be converted into potassium chlorate?
3. Write an account of the chemistry of sodium chloride. Your account should include a description of its chemical bonding, uses, occurrence, etc.
4. How would you distinguish between (*a*) sodium carbonate and sodium bicarbonate, (*b*) zinc carbonate and lead carbonate, (*c*) calcium carbonate and zinc carbonate?
5. Give an account of the general methods by which metals may be extracted from their ores.
6. Describe in some detail the extraction of (*a*) sodium, (*b*) aluminium, (*c*) zinc, (*d*) iron, (*e*) copper. What are the uses of these metals?
7. What do you know about the position of a metal in the electrochemical series and (*a*) its occurrence, (*b*) its extraction, (*c*) its reactivity with water, (*d*) the stability of its hydroxide and carbonate?
8. What do you see to happen, and what action occurs, when the following are heated: (*a*) potassium chlorate, (*b*) ferrous sulphate heptahydrate, (*c*) cupric carbonate, (*d*) cupric sulphate pentahydrate, (*e*) Gypsum, (*f*) sodium nitrate, (*g*) lead nitrate, (*h*) ammonium nitrite, (*i*) ammonium nitrate, (*j*) sodium hydroxide, (*k*) aluminium hydroxide?
9. What are limestone and gypsum? What important product can be

made from each? For what purposes are these products chiefly used?

10. Give the names and formulae of three common minerals containing calcium ions, and mention one use of each. What is the difference between permanent and temporary hardness, and what causes each type of hardness?

11. Name, and give the formula, of one naturally occurring compound of (*a*) magnesium, (*b*) zinc, (*c*) lead. Give one use of each metal and indicate the property of the metal on which the use depends. How can zinc be made from zinc oxide?

12. Describe experiments which illustrate the reaction of water or steam with (*a*) sodium, (*b*) calcium, (*c*) iron. Write balanced equations. How would you identify the products formed in (*a*) and (*b*)?

13. Describe the manufacture of aluminium. Give two uses of the metal. How does aluminium react with (*a*) oxygen, (*b*) hydrochloric acid, (*c*) sodium hydroxide, (*d*) ferric oxide?

14. Name, and give the formulae, of two ores of iron containing a mineral from which the metal may be extracted. Describe the extraction of iron. How may it be converted into steel by the Open Hearth process? Give a short account of the different types of steel.

15. Given metallic iron, describe how you would prepare (*a*) ferrous sulphate crystals, (*b*) ferric oxide, (*c*) anhydrous ferric chloride.

16. Describe the appearance of the three main oxides of lead. Describe what happens (if anything) when each oxide is warmed with (*a*) dilute nitric acid, (*b*) concentrated hydrochloric acid.

17. How does mercury occur and how may the metal be extracted? Give two uses of mercury. What is the action of heat on mercuric oxide.

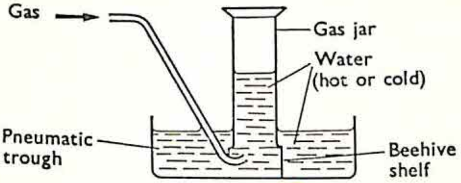
18. Give an account of the preparation and uses of cupric sulphate.

20 Collection and Drying of Gases

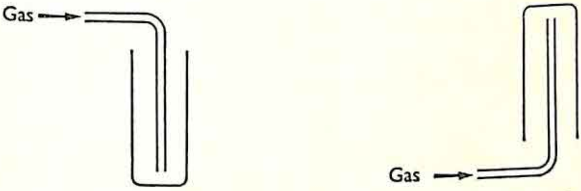
When gases are 'insoluble' in water, they are generally collected in gas jars 'over water', while soluble gases are collected by upward delivery (downward displacement of air) or downward delivery (upward displacement of air) depending on whether they are less or more dense than air. When full, the gas jars are sealed by a cover slip smeared with vaseline.

Small quantities of gases which are soluble in water are often collected 'over mercury'.

Collection of gases



(a) Over water for insoluble gases
For H_2, O_2, N_2, CO, NO (cold water)
For N_2O, H_2S (hot water)

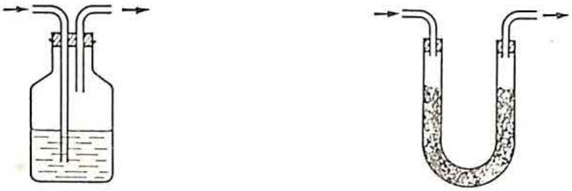


(b) Gases heavier than air; the approximate vapour densities being put in brackets
(*downward delivery*)
HCl (18), H_2S (17),
CO_2 (22), N_2O (22),
SO_2 (32), Cl_2 (36)
(*N.B.* approximate vapour density of air = 14.)

(c) Gases lighter than air; the approximate vapour densities being put in brackets
(*upward delivery*)
H_2 (1), NH_3 (9)

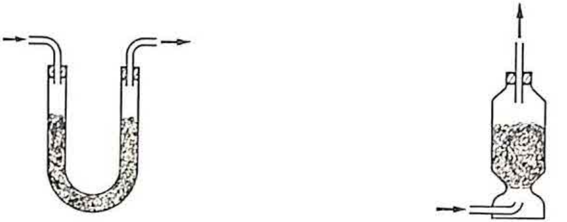
FIG. 20.1

Methods for drying gases



(a) Conc. H_2SO_4 in bottle

(b) Conc. H_2SO_4 soaked into pumice stone in a 'U' tube



(c) Anhydrous $CaCl_2$ or silica gel in a 'U' tube

(d) Quicklime in a tower

FIG. 20.2

Gas burette

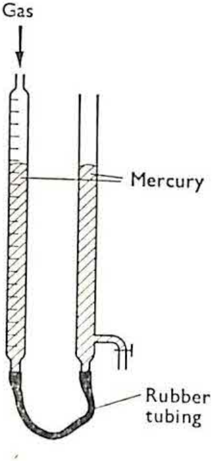


FIG. 20.3

If the gas is required dry, it must first be passed through (over) a suitable drying agent which does not react with the gas.

(*a*) Concentrated sulphuric acid: for all the common gases except NH_3 ($\rightarrow (NH_4)_2SO_4$), H_2S ($\rightarrow$ S), and NO_2 (absorbed to form a complex mixture of acids).

(*b*) Anhydrous calcium chloride: for all the common gases except NH_3 and H_2S.

(*c*) Silica gel: for all the common gases except NH_3.

(*d*) Quicklime: used almost exclusively for NH_3.

(*e*) Phosphoric oxide; for all common gases but is ordinarily used for removing last traces of moisture from a substance which is required in a particularly dry state.

A dried gas is not collected over water. If it cannot be collected by upward or downward delivery (i.e. O_2, N_2, CO, NO), it is best collected over mercury, using a gas burette (a special burette for the manipulation of volumes of gases, fig. 20.3).

(new standard, ^{12} C = 12·0000)

ELEMENT	SYMBOL	ATOMIC WEIGHT		ATOMIC NUMBER	MELTING POINT C	DENSITY (gg./cm^3)	VALENCY
		Exact	For calculations				
Mercury	Hg	200·60	—	80	*−39*	13·5	1, 2
Molybdenum	Mo	95·95	—	42	2620	10·2	3, 6
Neodymium	Nd	144·27	—	60	840	6·9	3
Neon	Ne	20·182	—	10	*−249*	(1·2)	—
Neptunium	Np	237	—	93	640	20·5	4, 5
Nickel	Ni	58·71	—	28	1455	8·9	2
Niobium	Nb	92·91	—	41	2500	8·6	3, 5
Nitrogen	N	14·008	14	7	*−210*	(0·8)	3
Nobelium	No	256	—	102	—	—	3
Osmium	Os	190·2	—	76	2700	22·5	4, 8
Oxygen	O	15·9993	16	8	*−218*	(1·1)	2
Palladium	Pd	106·4	—	46	1550	12·0	2, 4
Phosphorus	P	30·974	31	15	44	1·8	3, 5
Platinum	Pt	195·08	—	78	1773	21·5	2, 4
Plutonium	Pu	242	—	94	635	16·0	4
Polonium	Po	210	—	84	—	—	2
Potassium	K	39·100	39	19	62	0·9	1
Praseodymium	Pr	140·92	—	59	940	6·5	3
Prometheum	Pm	145	—	61	—	—	3
Protoactinium	Pa	231	—	91	—	—	5
Radium	Ra	226·04	—	88	700	5·0	2
Radon	Rn	222	—	86	*−71*	(4·4)	—
Rhenium	Re	186·22	—	75	3200	20·5	4, 7
Rhodium	Rh	102·91	—	45	1970	12·4	3
Rubidium	Rb	85·48	—	37	38	1·5	1
Ruthenium	Ru	101·1	—	44	1950	12·6	3, 8
Samarium	Sm	150·35	—	62	1300	7·7	3
Scandium	Sc	44·96	—	21	1200	2·5	3
Selenium	Se	78·96	—	34	220	4·8	2, 6
Silicon	Si	28·09	28	14	1420	2·4	4
Silver	Ag	107·876	108	47	960	10·5	1
Sodium	Na	22·991	23	11	97	0·9	1
Strontium	Sr	87·63	—	38	774	2·6	2
Sulphur	S	32·065	32	16	119	2·1	2, 6
Tantalum	Ta	180·95	—	73	3000	16·6	5
Technetium	Tc	99	—	43	—	—	4, 7
Tellurium	Te	127·61	—	52	450	6·2	2, 6
Terbium	Tb	158·93	—	65	330	—	3
Thallium	Tl	204·38	—	81	302	11·9	1, 3
Thorium	Th	232·04	—	90	1845	11·2	4
Thulium	Tm	168·94	—	69	—	—	3
Tin	Sn	118·70	—	50	232	7·3	2, 4
Titanium	Ti	47·90	—	22	1800	4·5	3, 4
Tungsten	W	183·86	—	74	3370	19·3	6
Uranium	U	238·07	—	92	1133	18·7	4, 6
Vanadium	V	50·95	—	23	1710	6·0	3, 5
Xenon	Xe	131·3	—	54	*−112*	(3·5)	—
Ytterbium	Yb	173·04	—	70	1800	—	3
Yttrium	Y	88·92	—	39	1490	5·5	3
Zinc	Zn	65·38	65	30	419	7·1	2
Zirconium	Zr	91·22	—	40	1860	6·4	4

ATOMIC WEIGHTS AND PHYSICAL PROPERTIES, 1961

ELEMENT	SYMBOL	ATOMIC WEIGHT		ATOMIC NUMBER	MELTING POINT °C	DENSITY (gg./cm^3)	VALENCY
		Exact	For calculations				
Actinium	Ac	227	—	89	—	—	3
Aluminium	Al	26·98	27	13	660	2·7	3
Americium	Am	243	—	95	850	11·7	3
Antimony	Sb	121·76	—	51	630	6·7	3, 5
Argon	A	39·942	—	18	*−189*	(1·4)	—
Arsenic	As	74·91	—	33	(814)	5·7	3, 5
Astatine	At	211	—	85	—	—	1
Barium	Ba	137·36	137	56	725	3·5	2
Berkelium	Bk	249	—	97	—	—	3
Beryllium	Be	9·013	—	4	1280	1·8	2
Bismuth	Bi	209·00	—	83	271	9·8	3, 5
Boron	B	10·82	—	5	2300	3·3	3
Bromine	Br	79·913	80	35	*−7*	3·1	1
Cadmium	Cd	112·41	—	48	321	8·6	2
Caesium	Cs	132·91	—	55	28	1·9	1
Calcium	Ca	40·08	40	20	842	1·5	2
Californium	Cf	249	—	98	—	—	3
Carbon	C	12·011	12	6	3500	3·5	4
Cerium	Ce	140·13	—	58	800	6·7	3, 4
Chlorine	Cl	35·455	35·5	17	*−101*	(1·9)	1
Chromium	Cr	52·01	52	24	1890	7·2	3, 6
Cobalt	Co	58·94	—	27	1495	8·9	2
Copper	Cu	63·54	63·5	29	1083	8·9	1, 2
Curium	Cm	245	—	96	—	—	3
Dysprosium	Dy	162·51	—	66	—	—	3
Einsteinium	E	254	—	99	—	—	3
Erbium	Er	167·27	—	68	—	—	3
Europium	Eu	152·0	—	63	1150	—	3
Fermium	Fm	255	—	100	—	—	3
Fluorine	F	19·00	—	9	*−223*	(1·1)	1
Francium	Fr	223	—	87	—	—	1
Gadolinium	Gd	157·26	—	64	—	—	3
Gallium	Ga	69·72	—	31	30	5·9	3
Germanium	Ge	72·60	—	32	960	5·3	4
Gold	Au	197·0	—	79	1063	19·3	1, 3
Hafnium	Hf	178·50	—	72	1700	13·3	4
Helium	He	4·003	—	2	*−272*	(0·2)	—
Holmium	Ho	164·94	—	67	—	—	3
Hydrogen	H	1·0080	1	1	*−259*	(0·1)	1
Indium	In	114·82	—	49	156	7·3	3
Iodine	I	126·91	127	53	114	4·9	1
Iridium	Ir	192·2	—	77	2450	22·4	3
Iron	Fe	55·85	56	26	1535	7·9	2, 3
Krypton	Kr	83·80	—	36	*−157*	(2·2)	—
Lanthanum	La	138·92	—	57	826	6·2	3
Lawrencium	Lw	—	—	103	—	—	3
Lead	Pb	207·20	207	82	327	11·3	2, 4
Lithium	Li	6·940	—	3	186	0·5	1
Lutecium	Lu	174·99	—	71	—	9·7	3
Magnesium	Mg	24·32	24	12	651	1·7	2
Manganese	Mn	54·94	55	25	1260	7·2	2, 7
Mendelevium	Mv	256	—	101	—	—	3

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Differences								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Differences								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

ANTI-LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Differences								
											1	2	3	4	5	6	7	8	9
·00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
·01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
·02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
·03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
·04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
·05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
·06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
·07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
·08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
·09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
·10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
·11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
·12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
·13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
·14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
·15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
·16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
·17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
·18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
·19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
·20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
·21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
·22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
·23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
·24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
·25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
·26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
·27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
·28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
·29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
·30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
·31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
·32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
·33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
·34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
·35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
·36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
·37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
·38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
·39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
·40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
·41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
·42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
·43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
·44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
·45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
·46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
·47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
·48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
·49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

ANTI-LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Differences								
											1	2	3	4	5	6	7	8	9
·50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
·51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
·52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
·53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
·54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
·55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
·56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
·57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
·58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
·59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
·60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
·61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
·62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
·63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
·64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
·65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
·66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
·67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
·68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
·69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
·70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
·71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
·72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
·73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
·74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
·75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
·76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
·77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
·78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
·79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
·80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
·81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
·82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
·83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
·84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
·85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
·86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
·87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
·88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
·89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
·90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
·91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
·92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
·93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
·94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
·95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
·96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
·97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
·98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
·99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

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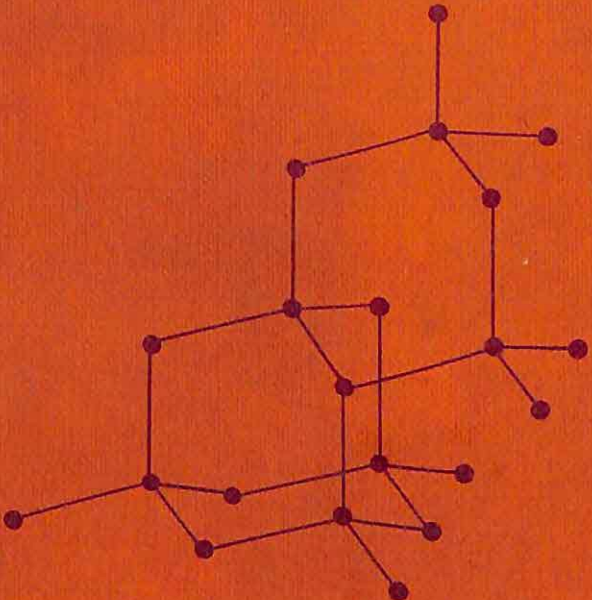

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